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AN EVALUATION OF CONTAMINANT RETARDATION MECHANISMS

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ABSTRACT

Understanding retardation mechanisms active in groundwater flow systems in crystalline rock is fundamental to the performance assessment of a deep nuclear waste repository. In this study, the retardation mechanisms are identified and described and the mathematical formulation and theory are discussed. In the second phase of the study, the I^- and Sr^{2+} tracer migration experiments performed at Finnsjon, Sweden, are interpreted assuming the identified retardation mechanisms are operational. Calculations are then performed using the interpreted retardation parameters to predict the migration of radionuclides from a generic geologic waste repository. These calculations show that a wide range of breakthrough curves are possible and that for the Finnsjon Sr^{2+} test matrix diffusion is the dominant retardation mechanism. The study also shows that the range of radionuclide breakthrough curves are specific to the individual tracer test conditions.

RÉSUMÉ

Pour évaluer le rendement de tout dépôt souterrain situé dans les roches cristallines, il est indispensable de bien comprendre les mécanismes actifs de retardement des systèmes des eaux souterraines. La présente étude indique et décrit, d'une part, les mécanismes de retardement et traite, d'autre part, de la formulation et de la théorie mathématiques. Dans la deuxième phase de l'étude, les expériences de migration des traceurs I^- et Sr^{2+} exécutées à Finnsjon, en Suède, sont interprétées en partant du principe que les mécanismes de retardement indiqués sont fonctionnels. Des calculs sont ensuite établis en utilisant les paramètres de retardement interprétés pour prévoir la migration des radionucléides hors d'un dépôt de déchets général dans les roches cristallines Ces calculs révèlent qu'une grande variété de courbes de passage est possible et que la diffusion de la matrice de l'épreuve Sr^{2+} de Finnsjon est le principal mécanisme de retardement. L'étude montre, en outre, que la gamme de courbes de passage de radionucléides est spécifique aux conditions individuelles de chaque épreuve de traceur.

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1. INTRODUCTION

1.1 BACKGROUND AND OBJECTIVES

The Canadian nuclear fuel waste management program is based on the premise that wastes can be safely isolated from man through deep underground disposal. The Canadian program has selected crystalline rock masses as the candidate rock type. An essential part of the program will involve evaluating the risk posed to man by the construction of such a facility. In order to evaluate these risks it is necessary to determine the mechanisms controlling the migration of radionuclides along various pathways to the biosphere. One of the major pathways which could transport radioactive material to the biosphere is leaching and dissolution of the waste by groundwater and subsequent movement through the groundwater system.

It is essential therefore that the factors controlling the movement of solute and groundwater in fractured crystalline rocks be well understood. One phenomena which is of paramount importance in describing the movement of solute in groundwater flow systems is retardation. Retardation is the term given to a collection of processes that both individually and collectively serve to slow the movement of solute relative to the actual groundwater velocity.

Retardation properties of crystalline rocks are typically quantified through interpretation of laboratory and field experimentation. Because the individual physical and chemical processes that comprise retardation are complex and generally not discernable in such experimentation, significant errors may be incorporated in predictive radionuclide transport calculations from a geologic repository based on interpretation of experimentation which has been performed at much smaller spatial and temporal scales. The Atomic Energy Control Board (AECB) commissioned this study to evaluate retardation mechanisms in crystalline rock and to assess the likely magnitude of errors in radionuclide migration calculations from a generic geologic repository introduced through incorrectly interpreting retardation mechanisms in field and laboratory tracer migration experiments.

1.2 SCOPE OF WORK

The study objectives were met through completion of the following tasks:

1. Identification and description of relevant retardation mechanisms in crystalline rocks;

2. Identification of mathematical formulation for each mechanism;

3. Discussion of the theory, assumptions and limitations of each mechanism;

4. Review, selection and analysis of tracer test data assuming various retardation mechanisms were operational;

5. Using "fitted" parameters from tracer test interpretation, long term radionuclide transport calculations were performed for a generic site assuming different retardation mechanisms were operational;

6. Discussion of the implications of the long term radionuclide transport calculations.

Section 2 of this report discusses the results of Tasks 1, 2, and 3. Sections 3 and 4 address Task 4 and Section 5 describes the findings of Task 5. Task 6 is discussed in both Sections 5 and 6.

2. RETARDATION MECHANISMS

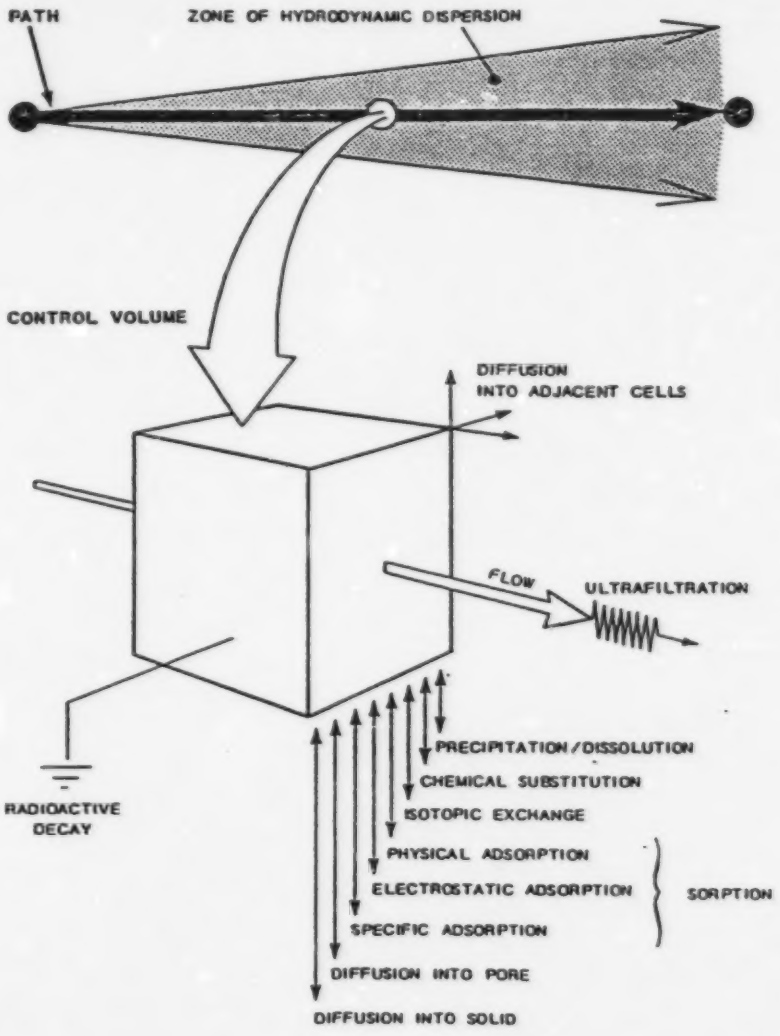
Retardation is the effect of all processes which hinder the mobility or migration of chemicals in solution or in suspension relative to the mobility or migration of water itself. In the context of radioactive waste disposal in geologic environments, consideration of retardation is an essential part of the assessment of the barrier provided by geologic formations.

Muller and Duda (1982), Nuclear Energy Agency (NEA, 1983) and Muller et al., (1983; 1984) summarize the different processes that comprise retardation. Figure 2.1 from Muller and Duda (1982) provides a conceptual model of the processes involved in retardation. Although all of the identified processes are interrelated and it is often not possible to distinguish between the processes in experimental studies, it is convenient to separate the processes to better understand the causes of retardation.

In this study and with reference to Figure 2.1, retardation mechanisms have been grouped according to four major processes. These are:

1) Precipitation/Co-precipitation - Dissolution
2) Sorption
3) Diffusion
4) Filtration.

Precipitation/co-precipitation - dissolution are bulk phase reaction processes which also include chemical substitution and isotopic exchange reactions. In the context of most radioactive waste disposal programs, sorption is the dominant chemical retardation mechanism and includes physical adsorption, electrostatic adsorption (ion exchange) and specific adsorption. Diffusion is the dominant physical retardation mechanism and includes pore diffusion, surface diffusion and solid diffusion. Diffusion into immobile porosity within fractures and within the rock matrix is included as part of pore diffusion. Filtration, or ultrafiltration, describes the physical retardation process by which the geologic medium preferentially retains solute over water within the pore fluid.



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CONCEPTUAL MODEL OF PROCESSES INVOLVED IN RETARDATION (AFTER MULLER AND DUDA, 1982)

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FIGURE 2.1

Filtration is significant for molecular aggregates such as colloids, microorganisms and organic complexes. Hydrodynamic dispersion and radioactive decay are not considered retardation mechanisms in the context of this study. The following parts of Section 2 provide descriptions, mathematical formulations and discussions of the theory of the retardation mechanism identified above.

Retardation is defined relative to the transport of a perfect (nonsorbing or conservative) tracer which describes the transport of water itself. In a simple one-dimensional steady flow system the transport of a conservative species is described by the advection-dispersion equation (Freeze and Cherry, 1979):

$$D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \qquad (2.1)$$

where: C = concentration of solute;
D_L = coefficient of hydrodynamic dispersion in the longitudinal or flow direction;
v = the average interstitial groundwater velocity;
x = curvilinear coordinate along a flow line;
t = time.

2.1 PRECIPITATION/CO-PRECIPITATION - DISSOLUTION

2.1.1 Description

Precipitation of an aqueous species will occur when the ion activity product (IAP) of its dissolved components exceeds the solubility product (K_{sp}) of the solid. Conversely, dissolution of a solid phase will occur when the solubility product of the solid exceeds the ion activity product of its dissolved components. If these processes are truly reversible they may be legitimately viewed as a retardation mechanism. If these processes are irreversible they should more appropriately be viewed as a source reduction or removal mechanism.

Special cases of precipitation include chemical substitution and isotopic exchange. Chemical substitution reactions are those reactions in which an aqueous phase atom of one element replaces a solid phase atom of a second element. This process is distinguished from ion exchange in that chemical substitution involves the breaking/forming of chemical bonds. Examples of chemical substitution processes include americium replacement on the surface of phosphate minerals and strontium replacement of calcium in carbonate minerals surfaces (NEA, 1983).

Isotopic exchange (Muller et al., 1983) is the process by which an isotope of an element in a solid phase is replaced by another isotope of the element in solution. In the context of radioactive waste migration the aqueous phase isotope is usually radioactive and the solid phase isotope is usually stable. Examples of isotopic exchange include the exchange of ^{14}C for ^{12}C in carbonate minerals.

Co-precipitation is the precipitation of a compound in conjunction with one or more components, frequently under conditions that would not normally render the compound insoluble. Bruno and Sandino (1987) recognize four types of co-precipitation:

1) isomorphous mixed crystal formation;
2) anomalous mixed crystal formation;
3) adsorption;
4) occlusion.

The first two types represent various degrees of solid solution. In the first, isomorphous mixed crystal formation, the solid phase constituents have similar properties, whereas in the anomalous mixed crystal category, this is not the case. Adsorption onto the surface of a precipitate represents the third type of co-precipitation mechanism. Occlusion, a special case of adsorption in which the adsorbed species are subsequently covered with other crystal planes, comprises the last mechanism.

The rate and extent of co-precipitation is dependent upon the ionic charge and size of substituting ions, temperature, and the concentration of the minor components.

2.1.2 Mathematical Formulation

Because of the highly complex and coupled nature of the chemical processes governing precipitation/dissolution reactions, computer models (or codes) must typically be used in the evaluation of these processes. Ion speciation/solubility codes (e.g., WATEQ, MINEQL, etc.) calculate activities of species in solution according to mass action laws and based on the chemical composition of the solution. Saturation indices for a variety of minerals can then be calculated provided the thermodynamic data required for the calculation of equilibrium solubility constants are known. More sophisticated reaction path-tracking codes (e.g., PHREEQE) allow for the transfer of mass into or out of solution and incorporate this effect on mineral precipitation or dissolution (Miller, 1983).

The incorporation of a trace element into a solid phase through co-precipitation can be described by partitioning theory (McIntire, 1963; Kinsman, 1969). If equilibrium is attained between the bulk of the solid solution and the aqueous phase, then the system follows the Berthelot-Nernst homogeneous distribution law:

$$D_t = \frac{(m_t/m_c)_s}{(m_t/m_c)_l} \qquad (2.2)$$

where:
- m = moles
- t = substituting element
- c = major element
- l = solution
- s = solid
- D_t = distribution coefficient.

If equilibrium is only achieved between the surface of the solid and the aqueous phase then the system follows the Doerner-Hoskins logarithmic law:

$$\log\left(\frac{m_t}{m_c}\right)_l = K \log\left(\frac{m_t}{m_c}\right)_s \qquad (2.3)$$

where: K = equilibrium partition coefficient.

If the material on the solid phase is treated with an activity as an aqueous species, equilibrium constants may be used to describe the partitioning of solute during precipitation, chemical substitution or isotopic exchange reactions (Muller et al., 1983).

In the special case of isotopic exchange, isotopic fractionation factors may be used to determine equilibrium constants for specific reactions (Muller et al., 1983). For example, in the case of exchange of radiocarbon, ^{14}C, in solution for stable ^{12}C carbon in calcite the exchange relation is:

$$Ca^{12}CO_3 + {}^{14}CO_3^{2-} \rightleftharpoons Ca^{14}CO_3 + {}^{12}CO_3^{2-} \qquad (2.4)$$

and the equilibrium constant, K_e is:

$$K_e = \frac{\left[Ca^{14}\ CO_{3_s}\right]\left[{}^{12}CO_3^{2-}\right]}{\left[Ca^{12}\ CO_{3_s}\right]\left[{}^{14}CO_3^{2-}\right]} \qquad (2.5)$$

Because the isotope enrichment factor, α_{as} in the aqueous - solid direction of exchange is defined as:

$$\alpha_{as} = \frac{r_a}{r_s} \qquad (2.6)$$

where: r_a = abundance ratio of rare heavy isotope in a phase and
r_s = abundance ratio of a common lighter isotope in a phase.

The bracketed quantities in (2.5) may be concentrations as well as thermodynamic activities, (2.5) may be written as:

$$K_e = \frac{r_a}{r_s} = \alpha_{as} \qquad (2.7)$$

In the case of reaction (2.4) the isotopic fractionation factor α_{as} between carbonate ion and calcite is 0.994. If exchanged and unexchanged phases are treated as aqueous species, reaction path simulation codes can be used to quantify the concentrations of isotopically exchanged species.

2.1.3 Discussion of Theory

The total maximum concentrations of actinides and fission products in solution are determined by solubility-limiting solid phases and the concentrations of potential complexing agents. Solubility limitations cannot maintain concentrations below regulatory maximum permissible concentrations for most fission products (Krauskopf, 1984), although precipitation of $SrCO_3$ and $SrCO_4$ may have to be considered in the interpretation of Sr tracer test data (Gustafsson and Klockars, 1984). However, in general, solubility controls, and consequently precipitation/dissolution as a retardation mechanism, are important mainly for the actinides and technetium.

The solubility of most actinides is widely variable since it is a function of the redox potential of the solution, pH (which controls the degree of hydrolysis) and total carbonate concentration (which defines carbonate complexation). Maximum actinide solubilities have been calculated assuming actinide oxides (except for Am) are the solubility limiting phases (Allard, 1983; KBS, 1983). These results are summarized in Table 2.1. Because solubility is always dependent on the crystal form of the solid, total solubilities could be several orders of magnitude greater than shown in Table 2.1 if metastable 1,4 actinide hydroxides (e.g., Th $(OH)_4$, $U(OH)_4$, $Np(OH)_4$, and $Pu(OH)_4$) are, in fact, the solubility-limiting phases.

Table 2.1 Solubilities for Actinides and Technetium in Groundwater (Solubility-limiting phases are given in parenthesis) (Modified after KBS, 1983)

Element	Maximum Concentration (ug/L) Reducing	Oxidizing
Tc	0.2 (TcO_2)	high (not solubility limited relative to dissolution rate of U oxide)
Am	10^2 ($Am_2(CO_3)_3$)	10^2 ($Am_2(CO_3)_3$)
Np	1 (NpO_2)	probably 10^4 for $Na_{2x-1}NpO_2(CO_3)_x$ where x = 0.8 to 1.0
Pu	10 (PuO_2, $Pu_2(CO_3)_3$)	1 PuO_2
Th	0.4 (ThO_2)	0.4 (ThO_2)
U	10 (UO_2)	high (limited by supply of carbonate), solubility limiting solid uncertain

It is clear from Table 2.1 that under reducing conditions the solubility of Tc, U and Np are at a minimum. This is consistent with the work of Bondietti and Frances (1979) who found that mobile TcO_4^- and NpO_2^+ can be chemically reduced to less soluble oxidation states (probably TcO_2 and NpO_2) in the presence of some igneous rocks. Cleveland et al. (1983) have demonstrated that Pu and Np solubilities are limited in reducing, high sulphate waters, however they were unable to offer a solubility or sorption control for this behaviour.

Co-precipitation of actinides such as Pu^{3+} may be an important retardation process if U that is initially dissolved from spent fuel is reprecipitated in the geosphere as U oxide or hydroxide ($U(OH_4)$) (Bruno et al., 1986). Initially the incorporation of the actinide on the U solid phase could be described by the logarithmic distribution law. However, upon aging of the precipitate, equilibrium between the entire solid phase and solution could be attained in which case the Berthelot-Nernst homogeneous law would have to be used. The overall effect of aging is to decrease the degree of coprecipitation.

Co-precipitation of fission products on ferric oxyhydroxides may also be important (Walton, 1986) although distinguishing this process from true sorption is problematic (Grondin and Drew, 1988). Aging and conversion of the amorphous ferric oxyhydroxide to crystalline Fe_2O_3 can fix sorbed fission products through occlusion in the Fe_2O_3 or as separate iron-radionuclide phases.

Chemical substitution and isotopic exchange reactions may be slow, only partly reversible, highly solute selective, temperature dependent and highly dependent on concentrations of solute. As with precipitation and co-precipitation, chemical substitution and isotopic exchange processes are difficult to distinguish from sorption under experimental conditions. Thus, although approaches for modeling these reactions have been developed (Muller et al., 1983), the inability to distinguish the occurrence of these reactions in most experimental migration experiments renders such approaches of limited practical use.

2.2 SORPTION

In general, the dominant chemical retardation mechanism is sorption, a process that removes species from solution and adsorbs them onto solid surfaces. Three types of sorption have been recognized, namely physical adsorption, electrostatic adsorption (ion exchange), and specific adsorption.

2.2.1 Description

Physical adsorption is due to relatively undirected and nonspecific forces of attraction between a solute and the adsorbing substrate. Hydrogen bonding and van der Waals forces of attraction are primarily responsible for physical adsorption. This process is rapid, reversible, and largely independent of temperature, the chemical composition of the sorbent, and the ionic strength of the solution. However, the pH of the solution and the concentration of complexing agents are important influences on physical adsorption. This process is the primary control on the mobility of neutral actinide hydroxy complexes.

Electrostatic adsorption is due to coulombic forces of attraction between charged solute species and a sorbent of opposite charge. This process is rapid, generally reversible, and slightly dependent on temperature, but strongly dependent on the composition of the sorbent and the composition and ionic strength of the solution.

The surface charge of the sorbent is produced either by interior lattice charge effects or by specific adsorption of potential determining ions on the surface. Interior lattice charge effects are most important in layered silicates such clay minerals and micas. Because these charge effects are not related to solution chemistry and are independent of pH (assuming mineral stability with respect to pH), the surface charge effect is constant. However for some sorbents, such as hydrous oxyhydroxides, the surface charge is determined by the adsorption of potential determining ions. When these ions are mainly H^+ and OH^- there is a pH at which the surface of the sorbent has a net charge of zero. This is known as the pH of the "zero point of charge" (ZPC). At pH values below the ZPC the surface is positively charged and acts as an anion exchanger; at pH values above the ZPC the surface is negatively charged and acts

as a cation exchanger. Therefore, ions adsorbed because of electrostatic forces are referred to as "ion exchanged" since their adsorption is accompanied by desorption of other ion species (of the same charge) from the surface.

Ion exchange is a major control on the migration of cation fission products such as ^{90}Sr and ^{137}Cs (Lieser and Peschke, 1982). Actinide cations and their oxides, such as Am^{3+}, NpO_2^+, and PuO_2^+, as well as cation complexes ($Am(CO_3)^+$, $Am(OH)^{2+}$, etc.), will also be subject to ion exchange processes.

Ion exchange can also include anion exchange, although in soils, sediments and rocks this is generally a minor process (Ames and Rae, 1978). Anions may experience repulsion from the predominately negatively charged medium, causing them to migrate at a velocity higher than that of the groundwater. Such an effect is known as anion exclusion.

Specific adsorption occurs when trace concentrations of sorbate occupy the relatively small number of sites of opposite charge that are present on a sorbent surface regardless of the net surface charge. It may also result by the sorbate ion inducing the formation of surface sites of opposite charge when adsorbed. For example, $UO_2(OH)^+$ is almost totally adsorbed onto ferric oxhydroxide surfaces having net positive charges. Specific adsorption is probably the most important kind of adsorption for trace radionuclide species in natural waters (Muller et al., 1984).

The kinetics of specific adsorption are highly variable (i.e., slow or rapid), being dependent on temperature, the composition of the sorbent and the ionic strength of the solution.

Chemisorption, which involves the chemical bonding of the sorbate to sorbent, is not true adsorption but rather a special case of precipitation.

2.2.2 Mathematical Formulation

Equilibrium sorption of a solute onto a solid phase may be modeled using simple distribution coefficients or more complex multiple parameter isotherm models. The distribution coefficient (Kd) is an empirical parameter

expressing the ratio of solute adsorbed per unit mass of solid (S), to the equilibrium solute concentration of sorbate, (C):

$$Kd = S/C \tag{2.8}$$

In fractured low-permeability rocks, where fluid flow is principally through fractures, the distribution coefficient is more commonly expressed as the ratio of solute adsorbed per unit area of solid to the equilibrium solute concentration of sorbate (i.e., Ka).

Assuming equilibrium conditions and reversibility the Kd or Ka distribution coefficients can be used to define a retardation factor (R) that expresses the ratio of the interstitial velocity of the groundwater, (v) to the effective velocity of the sorbate (v_s).

$$R = \frac{v}{v_s} \tag{2.9}$$

For a porous media system in which sorption may be described by an isotherm, a volume-based retardation factor may be defined as:

$$R = 1 + \frac{\rho}{n}\frac{\partial S}{\partial C} \tag{2.10}$$

which, for the case of a linear isotherm, reduces to:

$$R = 1 + \frac{\rho}{n} Kd \tag{2.11}$$

where ρ is bulk mass density of porous media and n is porosity. For flow in fractures a surface-based retardation factor may be defined as:

$$R = 1 + \frac{Ka}{b} \tag{2.12}$$

where b is half of the width of the fracture.

More complex multiple parameter isotherm models attempt to consider the dependence of electrostatic and specific sorption on sorbate concentration. Typically three isotherm models have been used to model concentration - dependent sorption, namely the Langmuir, Freundlich and Dubinin -Radushkevich models.

The equations for these isotherms are as follows:
Langmuir isotherm:

$$S = \frac{aS_mC}{1+aC} \qquad (2.13)$$

where: S = amount of solute adsorbed per unit mass of solid
S_m = maximum amount which can be adsorbed by the solid
C = equilibrium solute concentration of sorbate
a = constant related to the energy of adsorption.

Freundlich isotherm:

$$S = KC^N \qquad (2.14)$$

where: K,N = empirical constants

Dubinin - Radushkevich isotherm:

$$S = S_me^{-AE^2} \qquad (2.15)$$

where: $E = RT \ln (1 + 1/C)$
R = gas constant
T = temperature (°K)
A = constant.

Langmuir isotherms become linear at low sorbate concentrations and attempt to consider the finite sorption capacity of the solid. For radionuclide adsorption on to heterogeneous soils and sediments the Langmuir model has been observed to be a poor predictor of actual adsorption (NEA, 1983).

The Freundlich isotherm model has been most widely used in radionuclide sorption studies. When N=1, in Equation 2.14, the Freundlich equation becomes linear and corresponds to concentration independent retardation with the Freundlich constant K equal to Kd. However, in some situations the rate of sorption decreases with increasing solute concentration (N<1) as limited absorption sites become saturated. For concentration dependent retardation, the shape of solute breakthrough curves are very sensitive to the input solute concentration and the form of the sorption isotherm (McKinley and West, 1982). Melynk (1985) modeled contaminant migration with a nonlinear (N<1) Freundlich isotherm and determined that front-sharpening was a significant characteristic of such sorbate migration. The reversibility of the sorption process also strongly influences the shape of such breakthrough curves especially the amount of "tailing" in these curves (Toulhoat, 1985).

The Dubinin-Radushkevich isotherm is most valid for trace aqueous constituents, and has the ability to represent non-homogeneous adsorption sites and variable adsorption potential. Ames et al. (1982) successfully used this model to describe adsorption of uranium onto basalts and their weathering products.

Isotherm models only assess the effect of elemental concentration and cannot fully consider ion exchange. Mass action models have been used to describe ion exchange processes which, for ideal binary cation exchange, can be written as:

$$aN^{+b} + bMX \rightleftharpoons aNX + bM^{+a} \qquad (2.16)$$

where:
- M = major species in solution
- N = trace species in solution
- X = solid sorbent phase
- a = valence of major species
- b = valence of trace species

The equilibrium constant, K_e, for this reaction is:

$$K_e = \frac{[NX]^a\ [M^{+a}]^b}{[MX]^b\ [N^{+b}]^a} \qquad (2.17)$$

where the brackets indicate thermodynamic activities. Pearson (1981) has shown that if activities of the solid phase constituents are assumed to be proportional to their mass fractions, the equilibrium constant of equation (2.16) may be related to a distribution coefficient (Kd) by:

$$Kd = K_e\ Q\ (a_m^+/a_n^+)\ M_m \qquad (2.18)$$

where: Q = cation exchange capacity;
a = activity coefficient
M_m = mass concentration of major species.

Mass action models have been applied to complex heterogeneous water-rock systems by adding the adsorption capacities of the various solid sorbents present based on the mass fraction of each solid phase (NEA, 1983). However, mass action models cannot consider specific adsorption.

Empirical statistical models have been used to model sorption because of the inability of isotherm and mass action models to accommodate the large number of variables which influence sorption in natural systems. These models take the form of non-linear multinominal expressions such as:

$$Kd(Sr) = a(Ca^{2+}) + b(Na^+) + c(K^+) + d(Ca^{2+})(Na^+) + e(Ca^{2+})(K^+) + f(Na^+)(K^+) + g(Ca^{2+})(Na^+)(K^+) + h \qquad (2.19)$$

where: a to h are regression coefficients and
(Ca^{2+}), (Na^+), (K^+) = concentrations of the major competing cations

However, these models are of limited usefulness because of the large number of independent parameters (and the ranges in the values for these parameters) that can influence sorption in natural systems for which equations such as (2.19) must be formulated.

More sophisticated double layer or surface complexation models (Davis et al., 1978) can consider all the important independent variables influencing sorption and account for both ion exchange and specific adsorption. This approach develops a relatively complete set of mass action equations which also take into consideration the electrical double layer properties of the sorbent (NEA, 1983).

Miller (1983) and Muller et al. (1983) have proposed incorporating the surface complexation model into solute transport models based on ion speciation/solubility codes that allow for mass transfer into, or out of, solution. In these models, sorption is considered as a special case of the precipitation/ co-precipitation - dissolution model, as unsaturated solid phases are treated as aqueous species in the overall mass balance equation for that element.

All of the previously described distribution models and multiple parameter sorption models assume instantaneous equilibrium conditions exist between the sorbent and sorbate. Alternatively stated, this assumption implies that the sorption reaction rates are rapid relative to the observed time frame of the sorbate migration. While this assumption is likely appropriate for the time scales of radionuclide migration through geologic barriers, it may be inappropriate for interpretation of field and laboratory migration experiments with sorbing tracers conducted over much shorter time frames. To account for the importance of reaction rates and non-equilibrium conditions, several kinetic models have been proposed. The simplest model considers reversible sorption by first-order kinetics and is expressed as:

$$\frac{\partial S}{\partial t} = k_r (S_e - S) \qquad (2.20)$$

where k_r is a first-order reaction rate constant and S_e is the equilibrium concentration of sorbate on the geologic media. This equilibrium concentration may be determined from the equilibrium solute concentration, C, using the equilibrium linear, Langmuir, Freundlich or Dubinin-Radushkevich isotherms described in equations (2.8), and (2.13) to (2.15).

Hysteresis and different adsorption and desorption rates have been recognized in field and laboratory tracer and sorption tests (Goblet et al., 1979; Hodgkinson and Lever, 1983; McKinley and West, 1983). The governing differential equation describing two competing first-order reactions for sorption and desorption was described by Ogata (1964) and applied recently by Walton et al. (1986) and Melynk (1985):

$$\frac{\partial S}{\partial t} = k_s C - k_{ds} S \qquad (2.21)$$

where k_s is a first-order rate constant for sorption and k_{ds} is a first-order rate constant for desorption. Equation (2.21) can be related to Equation (2.20) by assuming a linear isotherm, expressing $S_e = KdC$ and recognizing that $Kd = k_s/k_{ds}$ (Valocchi, 1986)

More complex kinetic models including combinations of two or more mechanisms with first-order reactions have been proposed (Cameron and Klute, 1977; Selim et al., 1976) and successfully applied to describe ^{90}Sr migration in a sandy aquifer at Chalk River, Ontario (Melynk et al., 1983) and at Rhode Island (Kipp et al., 1986).

Complexation of radionuclides by organic ligands may greatly increase the mobility of radionuclides through the formation of anionic complexes (Champ et al. 1984). Toulhoat (1985) has conducted tracer tests on fractured granite using uranyl carbonate and Th and lanthanide - EDTA complexes and found that when the tracer is complexed non-linear sorption laws govern interactions. Furthermore, if the complex itself can interact with the substrate the reversibility of the sorption reactions can be affected. Complexation can be modelled by replacing the Freundlich constant K with K' which can be referred

to as a global sorption constant that reflects sorption and complexation (Toulhoat, 1985).

2.2.3 Discussion of Theory

Sorption processes are dependent to varying degrees on the pH, E_H, temperature and ionic strength of the solution, the concentration and speciation of the sorbate, the concentration of complexing or competing species, the properties of the sorbent (mineralogy, chemistry, surface properties, crystallinity, surface/volume ratio, etc.) and time. Because experimentally determined distribution coefficients constitute the sum of all contributions from different sorption processes they are specific to the physical/chemical conditions under which they were measured. In spite of these limitations the isotherm approach to quantifying sorption is widely used by many investigators due to its ease of measurement and relatively straight forward incorporation into mass transport models. Representative distribution coefficients for radionuclides in granitic bedrock-ground water systems are listed in Table 2.2 (KBS, 1983). Note that these values are only representative for relatively fresh ground waters. Because the waste repository will almost certainly be invaded by saline water or brine following closure the Kd values for Sr and Cs in Table 2.2 are likely too high. On the other hand, the effect of possible high exchange capacity fracture infilling minerals has not been considered in Table 2.2.

Anderson and Allard (1983) compiled a comprehensive summary of available Kd measurements for fission products on various geologic materials. These authors concluded that because Sr and Cs are present in ground waters as uncomplexed cations, their sorption is controlled primarily by electrostatic adsorption (i.e. ion exchange). Sorption of Sr is strongly pH dependent (Landstrom et al., 1982). Although Cs sorption is mainly a cation exchange process (Torstenfelt et al., 1982), it is also selectively and irreversibly sorbed to illite because of its accommodation in interlayer sites (Jackson and Inch, 1980; Olsen et al., 1986). This may partially account for the nonlinear Cs sorption on crushed granite rock samples observed by Skagius et al. (1982).

Table 2.2 Distribution Coefficients, Kd, for Radionuclides in Granitic Bedrock-Groundwater Systems. (Low salt content, reducing conditions). Values for oxidizing conditions are given within parenthesis for the redox-sensitive elements (from KBS, 1983)

Element	Distribution coefficient, m^3/kg	
	Values Used by KBS	Best Estimate
Co	0.2	
Ni	0.2	
Sr	0.004[a]	
Zr	4	
Nb	4	
Tc	0.05 (0.0002)	
I	0	
Cs	0.05[a]	
Lanthanides	5	
Ra	0.1[a]	
Th	5	13[b]
Pa	5	23
U	5 (0.01)	>13[b] (0.06)[c]
Np	5 (0.01)	>13[b] (0.03)
Pu	5 (3)	6 (4.3)
Am	5	6

[a] considerably higher values can be obtained for high-capacity minerals, and even lower values for some low-capacity minerals, e.g. quartz. The distribution coefficient can be assumed to decline in proportion to the concentration of competing positive ions in the water which can give lower values in waters with high salt content (higher than 1,000 mg/L)

[b] Pertains to tetravalent uranium and neptunium; the value for thorium has been postulated as the minimum value.

[c] Pertains to hexavelant uranium: at very low uranium contents (below 10^{-10} M), values up to one order or magnitude higher can be obtained.

For Co and Ni, sorption is related to their hydrolysis and the formation of cationic hydrolysis products. Consequently their sorption is also strongly pH dependent. Technetium and iodide exhibit little sorption primarily because of their anionic speciation.

Because electrostatic adsorption is strongly dependent on the nature of the sorbent, sorption of fission products in crystalline rocks will be controlled by secondary fracture minerals. In Canada, calcite and chlorite are generally the two most abundant fracture minerals in rocks from the AECL research areas (Stone and Kamineni, 1982; Ejeckam et al., 1985; Kamineni et al, 1984; Dugal et al, 1979; Dugal and Kamineni, 1988; Bottomley, 1987 and 1988) as well as in Sweden (Landstrom et al. 1982; Tullborg, 1985; Torstenfelt et al., 1982; Nordstrom, 1983; Gustafsson and Klockars, 1984). Several studies have shown that calcite has a very low sorption capacity for both Sr and Cs and does not significantly increase their sorption over that provided by the bulk rock mineralogy (Gustafsson and Klockars, 1984; Torstenfelt et al., 1982; Muuronen et al., 1985; NEA, 1983). Chlorite and other layered silicates, such as sericite and biotite, have large sorption capacities for fission products. Clearly the distribution of mineral sorbents on fracture surfaces will have a major influence on fission product migration and on the choice of model Kd values used in solute transport codes to predict this migration over time scales of 10,000 years.

In contrast to the fission product elements which usually display electrostatic adsorption, sorption of the actinide elements is usually by physical adsorption processes. Consequently the nature of the sorbent is much less important for sorption of the actinides than it is for fission product elements. Sorption of several of the actinides is controlled by their speciation which in turn is determined by the ground water pH and E_H. Actinide speciation and sorption is discussed in detail by Allard (1982; 1983).

It is a characteristic of the actinide elements that different actinides in the same oxidation state have similar chemical properties whereas oxidation states of the same actinide have completely different properties. For example PuIII, AmIII and CmIII behave similarly as do NpIV and PuIV. Actinide complexation by hydroxide and carbonate ligands is a major control on actinide

sorption. The tri- and tetra-valent actinides experience increasing hydrolysis and sorption with increasing pH (to 9 or 10) and sorption maxima occur when neutral hydroxy complexes predominant. This sorption is physical adsorption and results in the sorption of the actinides in consecutive layers on the sorbent. It is reversible, rapid, highly dependent on pH, but relatively independent of nuclide concentration and sorbent composition.

Table 2.3 lists the predominant species of the actinide elements under oxidizing and reducing conditions. In saline waters other species may predominate, such as $AmCl^{2+}$ or $AmSO_4^+$. At high pH (>9) sorption decreases as anionic hydroxy and carbonate complexes become more abundant. For example, U is extremely soluble under oxidizing conditions as the anionic complex $(UO_2)_3(CO_3)_6^{6-}$. Although physical adsorption is the most important sorption process, the fact that sorption decreases as anionic complexes predominate indicates electrostatic interactions must also be significant.

Specific adsorption of radionuclides on iron oxyhydroxides (Hsi, 1981) may be important because these sorbents are common fracture coatings in granitic plutons. Furthermore, these sorbed elements may eventually become incorporated into the lattice of Fe_2O_3 upon aging and would be non-exchangeable. This process has been demonstrated for Am, Ce, Se, Sb, Sn, Co and Mn (Walton, 1986).

Sorption kinetics and reversibility are important considerations in the interpretation of radionuclide migration. Walton et al. (1983) developed a dimensionless sorption rate parameter β for assessing the influence of sorption kinetics on radionuclide migration. This parameter is defined as:

$$\beta = kt_w A/V \qquad (2.22)$$

where: k = first-order sorption rate constant
t_w = water transit time between two observation points
A/V = ratio of sorbent surface area to groundwater volume.

Table 2.3 Predominant Actinide Species in Low Salinity, Crystalline Rock Groundwaters

Element	OXIDIZING		REDUCING	
	low pH to neutral	high pH	low pH to neutral	high pH
Am (+3)	Am^{3+}	$Am(CO_3)^+$, $Am(CO_3)_2^-$ $Am(OH)^{2+}$, $Am(OH)_2$, $Am(OH)_3$	same as for oxidizing	
Np (+4 or +5)	NpO_2^+	$Np(OH)_4^o$, $NpO_2(CO_3)_2^{3-}$ $NpO_2(CO_3)_3^{5-}$	$Np(OH)_4$	$Np(OH)_4$ $Np(OH)_5^-$
Pu (+3, +4, rarely +6)	PuO_2^+	$Pu(OH)_4$, $Pu(OH)_5^-$	Pu^{3+}, $Pu(CO_3)^+$ $Pu(OH)_4$	$Pu(OH)_4$ $Pu(OH)_5^-$
U (+4, +5, +6)	$(UO_2)_3(CO_3)_6^{-6}$ $UO_2(OH)_5^{5-}$	$(UO_2)_3(CO_3)_6^{-6}$ $UO_2(OH)_5^{5-}$	$U(OH)_4$ UO_2^+	$U(OH)^-_5$ $UO_2(CO_3)_x^{2-2x}$ where x = 1 to 3
Th (+4)	$Th(OH)_4$	$Th(OH)_4$	$Th(OH)_4$	$Th(OH)_4$

The degree of retardation provided by a particular chemical mechanism is related not only by equilibrium distribution parameter (i.e., Kd or other sorption isotherms) but also by the sorption rate parameter β (Walton et al., 1983). Table 2.4 summarizes the effect of the sorption kinetics on radionuclide migration expressed as the β parameter. Table 2.4 indicates a pulse injection of radionuclide will travel with the groundwater for $0.1 < \beta < 1$ whereas complete retardation according to equilibrium distribution parameters (e.g., Equation (2.11) and (2.12)) would occur only for $\beta > 100$. For intermediate values of β, "kinetic" peak broadening and tailing occurs.

Partial irreversibility of radionuclide sorption has been interpreted in both field tracer tests and laboratory column experiments and expressed as different rate constants for sorption (k_s) and desorption (k_{ds}). While this approach recognizes partial irreversibility of sorption under particular experimental conditions, the mechanisms responsible for this phenomena are poorly understood. For example the low mass recovery in the Sr^{2+} field migration experiment at Finnsjon, Sweden has been interpreted to result from irreversible sorption (Gustafsson and Klockars, 1984; Hodgkinson and Lever, 1983). However the exact geochemical mechanisms responsible for this irreversibility could not be identified. Several mechanisms, including binding or co-precipitation with carbonates, binding by organic compounds and sorption by iron or manganese oxyhydroxides, are possible explanations.

2.3 DIFFUSION

2.3.1 Description

Diffusional processes are those processes in which chemical species move due to their kinetic energy in the direction of a concentration gradient. Because concentration gradients can be in a direction different from the direction of flow, diffusion can be considered a retardation mechanism.

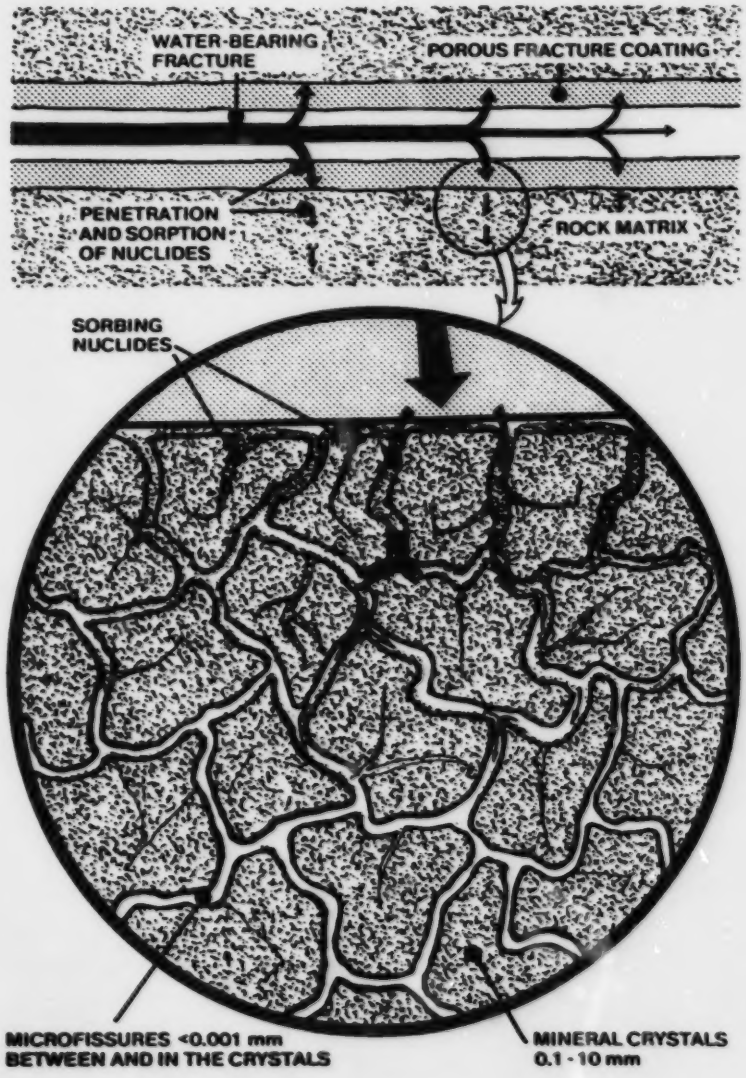
Table 2.4 Radionuclide Migration as a Function of Sorption Kinetics (after Melnyk, 1985)

Normalized Sorption Rate Constant	Characteristics of Radionuclide Migration
$\beta < 0.1$	No retardation. Effects of reaction are negligible on radionuclide migration.
$0.1 < \beta < 1$	No retardation but tailing occurs due to slow sorption/ desorption reactions.
$1 < \beta < 10$	Large kinetic broadening (dispersion) occurs. Double-peaked or bimodal elution curves may be produced. Velocity of migration changes during transport through the column. Some degree of retardation occurs.
$10 < \beta < 100$	Kinetic dispersion decreases as $\beta \rightarrow 100$. Migration is retarded by nearly the equilibrium amount.
$\beta > 100$	Reaction is in equilibrium. Complete equilibrium retardation occurs.

The general governing equations for diffusion are Ficks Laws. In hydrogeologic systems of low groundwater velocity, diffusion can be an important retardation mechanism and may be the dominant process retarding the transport of solute (Gillham and Cherry, 1982). In fractured, low-permeability rocks, three major types of diffusion process can be distinguished: pore diffusion, solid diffusion and surface diffusion.

Pore diffusion describes the diffusion of species into mobile (adjacent control volumes involved in fluid flow) and immobile pore spaces (those volumes of the pore space not actively involved in fluid flow). In fractured, low-permeability rock where the majority of fluid flow is within fractures, immobile porosity may exist within dead zones of the major water bearing fracture (Raven et al., 1988) and within the unfractured rock matrix that separates conductive fractures (Grisak and Pickens, 1980). Within conductive fractures a free water diffusion coefficient (D_o) is often used to describe diffusional processes. Free water diffusion coefficients for most major groundwater ions average 1-2 x 10^{-9} m^2/s at 25°C (Weast, 1984). Diffusion to immobile pore spaces through an irregular interconnected network of pores and microfissures occurs at a slower rate and is described by an effective diffusion coefficient (D_e). Effective diffusion coefficients for non-sorbing species are reported as 10^{-14} to 10^{-12} m^2/s (Bradbury and Green, 1985, Skagius and Neretnieks, 1986a). Figure 2.2 from KBS (1983) schematically shows the diffusion and sorption of radionuclides from a conductive fracture into adjacent porous fracture infilling minerals and a porous rock matrix.

The geometry of pore diffusion can be variable and is controlled by the geometry of the fracture flow path (i.e., parallel plate flow or channelled flow) and the fracture geometry. Slab geometries have been considered for diffusion from fractures exhibiting parallel plate flow, whereas cylindrical geometries have been suggested for channelled flow (Rasmuson and Neretnieks, 1986).


WATER-BEARING FRACTURE
POROUS FRACTURE COATING
PENETRATION AND SORPTION OF NUCLIDES
ROCK MATRIX
SORBING NUCLIDES
MICROFISSURES <0.001 mm BETWEEN AND IN THE CRYSTALS
MINERAL CRYSTALS 0.1 - 10 mm

Drawn by	Date
Checked by	Date
Revisions	Date

DIFFUSION AND SORPTION OF RADIONUCLIDES FROM A FRACTURE TO MICROFISSURES IN THE ROCK MATRIX (AFTER KBS, 1983)

INTERA Technologies

FIGURE 2.2

Solid diffusion is the process by which species diffuse into the solid grains or crystals which comprise the rock or geologic media. This diffusion process is treated in a manner analogous to pore diffusion, but is likely not as important a process because of the generally smaller solid diffusion coefficients which typically are six orders of magnitude smaller than free water diffusion coefficients. For example at 440°C the diffusion coefficient of Cu into Al is 5×10^{-15} m^2/s (Muller et al., 1983). The rate of the solid diffusion process, like most diffusion processes, is strongly temperature dependent. Moreover the driving force for solid diffusion does not directly include the concentration of a species in solution but rather the amount sorbed onto the solid of interest (Muller et al., 1983).

Surface diffusion is the process by which sorbed species are transported along sorption surfaces such as crystal or grain boundaries. Such processes have recently been proposed by Rasmuson and Neretnieks (1983) and Skagius and Neretnieks (1988) to explain rapid Cs and Sr diffusion rates that were higher than could be explained solely by pore diffusion. Rasmuson and Neretnieks (1983) summarize the available literature on surface migration processes, including surface diffusion, and conclude that surface diffusion can be an important transport mechanism at low solute concentrations and elevated temperatures. Skagius and Neretnieks (1988) observed that both pore and surface diffusion mechanisms acting in parallel were necessary to explain laboratory diffusion experiments using Cs^+ and Sr^{+2}. The surface diffusion process is treated in a manner analogous to pore diffusion, but as with solid diffusion, the net transport of sorbate occurs in response to a gradient in the chemical potential of atoms in the absorbed layer, not to a gradient in the concentration of pore fluids as assumed in Ficks laws.

2.3.2 Mathematical Formulation

In an aqueous isothermal system at uniform pressure, diffusion takes place in the direction of decreasing concentration, and the rate of transport per unit area of cross-section, F, is given by Fick's first law:

$$F = -D_o \frac{\partial C}{\partial x} \qquad (2.23)$$

where D_o is the diffusion coefficient. Fick's second law:

$$\frac{\partial}{\partial x}\left(D_o \frac{\partial C}{\partial x}\right) = \frac{\partial C}{\partial t} \tag{2.24}$$

gives the rate of change of concentration at a point in a one-dimensional system. Forms of (2.23) and (2.24) are widely used to describe diffusion processes in geological materials. The one dimensional form of (2.24), appropriate for a porous geologic material, is (Bradbury et al., 1982):

$$D_e \frac{\partial^2 C}{\partial x^2} = \alpha \frac{\partial C}{\partial t} \tag{2.25}$$

with $$D_e = D_o \tau \tag{2.26}$$

and $$\alpha = n + \rho Kd \text{ (assuming a linear sorption isotherm)} \tag{2.27}$$

where D_e = effective diffusion coefficient
τ = tortuosity factor
α = rock capacity factor.

The effective or intrinsic diffusion coefficient, D_e, is the coefficient in Fick's law which relates flux of solute per unit area of porous medium to the concentration gradient. The apparent diffusivity coefficient, D_e/α, describes time dependent diffusion. The rock capacity factor, α, relates concentration per unit volume of the medium to that in the water. For sorbing species in low porosity systems such as crystalline rock, α approximately equals Kd and (2.25) may be written as (Moreno et al., 1985):

$$\frac{D_e}{\rho Kd} \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \tag{2.28}$$

where Kd is the mass-based equilibrium distribution coefficient described earlier.

Equation (2.28) describes one-dimensional sorbing diffusional transport in a porous medium. In geologic media where there is negligible groundwater flow, (2.28) describes the overall transport of a sorbate in one dimension.

In dual porosity media where groundwater flow in one type of porosity such as fracture porosity is significant, (2.28) also describes the transfer of solute into an immobile second porosity such as a porous rock matrix under conditions of planar flow within the fractures. Under this slab geometry, (2.28) is coupled to the advective-dispersion equation (i.e., 2.1) describing flow and transport within the fracture through equality of solute concentration at the fracture-matrix interface. The solution to these two equations is provided through specification of boundary conditions including boundary conditions for the porous rock matrix.

If fluid flow within fractures occurs within discrete high permeability channels, diffusion from such channels is described by (2.28) expressed in radial coordinates (Rasmuson and Neretnieks, 1986):

$$\frac{D_e}{\rho K d} \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C}{\partial r}\right) = \frac{\partial C}{\partial t} \qquad (2.29)$$

Rasmuson and Neretnieks (1986) note that the diffusion flux across the surface of a cylindrical channel is greater than that for a semi-infinite slab, particularly at late times. This apparent increase in retardation of solute in the cylindrical channel is, however, offset for sorbing solute by the reduced surface area available for sorption with a cylindrical channel versus a planar fracture.

Under conditions where an immobile porosity may exist within parts of a fracture plane that otherwise conduct fluid, diffusional transport of solute may occur between the mobile (ϕ) and immobile ($1-\phi$) fractions of the total fracture pore space. The governing equation for one-dimensional non-reactive transport within the flowing sections of the fracture is based on (2.1) with additional terms to describe transport between mobile and immobile porosities (Coats and Smith, 1964):

$$D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \phi \frac{\partial C}{\partial t} + (1-\phi) \frac{\partial C_s}{\partial t} \quad (2.30)$$

where C = concentration in mobile fluid
C_s = concentration in immobile fluid and
other parameters are as previously defined.

Many researchers have assumed that mass transfer between mobile and immobile pore spaces follows a kinetic behaviour. The governing equation for the immobile fluid zone assuming a first-order exchange relation is (Lapidus and Amundson, 1952):

$$(1 - \phi) \frac{\partial C_s}{\partial t} = k (C - C_s) \quad (2.31)$$

where k is the first-order mass transfer rate coefficient describing diffusive equilibration between the mobile and immobile fluid phases. Bradbury and Green (1985) developed similar equations to (2.30) and (2.31) without the advective term to describe porous rock diffusion with interconnecting and dead end pores.

Considering equilibrium adsorption (2.30) and (2.31), the governing equations for an immobile/mobile porous system are (Van Genutchen and Wierenga, 1976):

$$D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \phi \frac{\partial C}{\partial t} + \rho p \frac{\partial S}{\partial t} + (1-\phi)\frac{\partial C_s}{\partial t} + \rho(1-p) \frac{\partial S_s}{\partial t} \quad (2.32)$$

and

$$(1-\phi) \frac{\partial C_s}{\partial t} + \rho(1-p) \frac{\partial S_s}{\partial t} = k (C - C_s) \quad (2.33)$$

where p is the fraction of total adsorption capacity of the solid assigned to the mobile fluid phase, (1-p) is the fraction assigned to the immobile fluid phase and S and S_s are the bulk mass-based concentrations of sorbate for the solid associated with the mobile fluid phase and immobile fluid phase, respectively. Complex analytical solutions to (2.32) and (2.33) have been derived for a linear (Kd) isotherm by Van Genutchen (1974).

Solid diffusion is typically modeled using Fick's laws with an appropriate solid diffusion coefficient and the recognition that the driving forces are the concentrations of sorbed species on the solids.

Surface diffusion of sorbing species has been modeled using Fick's laws with Langmuir and Freundlich isotherms (Skagius and Neretnieks, 1988). The governing equation for combined surface diffusion and pore diffusion is (Skagius and Neretnieks, 1988):

$$D_p \frac{\partial^2 C}{\partial x^2} + \frac{\rho D_s}{n} \frac{\partial^2 S}{\partial x^2} = \frac{\partial C}{\partial t} + \frac{\rho}{n} \frac{\partial S}{\partial t} \qquad (2.34)$$

where n is porosity, D_p is a pore diffusion coefficient equal to D_e/n, D_s is surface diffusion coefficient and S is the bulk mass-based concentration of sorbate described previously.

2.3.3 Discussion of Theory

The theoretical basis of diffusion is well established in the physical sciences through the use of Fick's laws. Although the theory is well established, the application of the theory in describing the retardation of solute in fractured low permeability crystalline rock over the large spatial and temporal scales relevant to the radioactive waste disposal problem is less certain.

Because the time frames of diffusion experiments need to be relatively long, assessment of diffusion processes in low permeability rock has been restricted principally to laboratory experiments with non-sorbing species using thin (generally less than 50 mm thick) rock specimens (Wadden and Katsube, 1982; Bradbury et al., 1982; Melnyk, 1983; Bradbury and Green, 1985; Skagius and Neretnieks, 1986) and fractured core samples (Neretnieks et al., 1982; Moreno et al., 1985).

The results of these experiments generally show that the theory adequately describes the experimental data assuming pore diffusion described by variations of (2.25) with effective diffusion coefficients (D_e) of 10^{-14} to 10^{-12} m^2/s (Skagius and Neretnieks, 1986a). The extent to which these laboratory results derived from tests performed on intact and fractured samples are representative of in situ conditions is not immediately clear. It is recognized that effective diffusion coefficients determined from laboratory tests may overestimate in situ conditions due to micro fissure porosity increases in the sample in response to stress relaxation during coring and sample retrieval. Skagius and Neretnieks (1986b) measured diffusivity reductions of 20-70% on restressed rock samples. Furthermore, enhanced porosities and effective diffusion coefficients are known to exist in the thin weathered surface of natural fractures (Bradbury and Green, 1985) and care must be exercised in extrapolating short-duration diffusion experiments which may measure only properties of the weathered surface to lower diffusivity, non-weathered rock.

In theory, the diffusion properties of the non-weathered rock will determine the retardation due to diffusion over the long time scales involved in radioactive waste disposal. The shorter times representative of most field tracer tests may not accurately estimate this effect. For example, effective diffusion coefficients reported by Neretnieks et al. (1982) and Moreno et al. (1985) from non-sorbing tracer migration experiments in natural fractures with water residence times of minutes to a few hours, reflect the diffusivity of the near surface weathered rock and any mineral infilling and immobile porosity present within the fracture. Assuming homogeneous conditions within the fracture and the adjacent rock matrix (i.e., for constant D_e) the penetration distance (d_p) of a tracer into the matrix can be approximated as (Hodgkinson and Lever, 1983):

$$d_p = \sqrt{4 D_e t/\alpha} \qquad (2.35)$$

where t is contact time and D_e and α are as previously defined. Equation (2.35) shows that for non-sorbing species with $\alpha = 0.01$ and $D_e = 1 \times 10^{-13}$ m^2/s, a penetration distance of 1.2 mm is determined for contact time of 10 h .

Recognizing the limitations of laboratory diffusion experiments, limited field experiments have been conducted and/or interpreted to estimate in situ effective diffusion coefficients for non-sorbing species. Such field estimates have been determined from interpretations of tracer migration experiments (Glueckauf, 1981; Hodgkinson and Lever, 1983; Moreno et al., 1983; Maloszewski and Zuber, 1985) or from in situ diffusion experiments (Birgersson and Neretnieks, 1982; 1984; Birgersson, 1988). None of the available tracer migration experiments have been of sufficient duration or with sufficient characterization of the flow path to consider the interpreted diffusivities as reliable. For example, Hodgkinson and Lever (1983) and Moreno et al. (1983) interpreted the Finnsjon I^- tracer test data of Gustafsson and Klockars (1981) and determined effective diffusion coefficients for I^- which were about two-three orders of magnitude greater than all available laboratory measurements. The higher diffusivities may reflect non-equilibrium effects within the flowpath (i.e., convective and diffusive transfer into stagnant zones in or adjacent to the flowpath) or enhanced diffusivity and porosity within the weathered rock surfaces in contact with the flowpath.

The in situ diffusion tests of Birgersson (1988) are the only field experiments to reliably quantify the diffusion processes of non-sorbing species. In these tests, uranine, Cr-EDTA and I^- were injected into Swedish granite for time periods of up to 3.5 years and cored rock samples were analyzed for tracer concentrations. Tracers were detected at radial distances up to 0.4 m from the injection hole for the 3.5 year experiment.

Pore diffusivities (D_p) calculated from this experiment ranged from 2×10^{-12} to 5×10^{-10} m^2/s which, with an average measured (matrix) porosity of 0.003 are equivalent to effective diffusion coefficients of 6×10^{-15} to 1×10^{-12} m^2/s, similar to laboratory experimental values. The experiments by Birgersson (1988) demonstrate that conservative species can migrate considerable distances into intact rock and that the rock matrix pore space can be a significant and accessible sink for such species.

The pore diffusion of sorbing species is less well documented and understood than for non-sorbing species. Because of the long observation times required, few meaningful sorbing diffusion experiments have been performed and the applicability of (2.28) in describing diffusion even with simple linear reversible sorption (i.e., Kd) has not been reliably demonstrated. Vandergraaf (1985) suggested that at low radionuclide concentrations, surface sorption dominates retardation and only at high solute concentrations, when surface sorption sites are saturated, does the rock matrix become accessible for diffusion and sorption. Vandergraaf (1985) observed virtually no diffusion of $^{137}C_s$ and marginal penetration of strontium into the rock matrix.

The rapid diffusion of sorbing species reported by Skagius and Neretnieks (1986) and explained by the incorporation of a surface diffusion process, suggests the simple pore diffusion model (2.28) is inadequate in describing sorbing diffusion and that the mechanisms of such diffusion are poorly understood. In fact, the experiments by Skagius and Neretnieks (1982, 1986a) demonstrate that effective diffusivity of strontium and cesium was greater than for the non-sorbing species, iodide, in contradiction to (2.28). Furthermore because different sorption isotherms were required to model the behaviour of sorbing species in various diffusion tests reported by Skagius and Neretnieks (1986a) there is the possibility that other time dependent processes (i.e., kinetics) affected the experimental results.

2.4 FILTRATION

2.4.1 Description

Filtration or ultrafiltration (Muller et al., 1983) is the mechanical retardation process by which the geologic medium preferentially retains solute over water within the pore fluid. Filtration is most significant for larger size molecular aggregates such as colloids, micro-organisms, organic complexes and some ions with large hydration spheres. Filtration may be a retardation mechanism for radioactive waste disposal because colloids, micro-organisms and organic complexes can serve as radionuclide carriers and transport nuclides as both charged and neutral species.

Colloidal transport is likely to be significant for Tc, Np and Pu (Avogadro and de Marsily, 1984) as these elements are expected to give rise to solid dispersed states and form colloids through the association of micro-colloids naturally existing in the groundwater or produced through corrosion of container material or by degradation of backfill material. Collodial transport has also been inferred for fission products such as ^{85}Sr (Landstrom et al., 1982) in attempting to explain early breakthrough of tracer in field migration experiments. Transport of radionuclides by micro-organisms and organic complexes is described by Mayfield and Barker (1982), West et al. (1982) and McKinley et al. (1986) but remains poorly understood. McKinley et al. (1986) suggested natural organic compounds and micro-organisms would not have a significant effect on radionuclide transport in the context of the Swiss program for disposal of high-level radioactive waste.

2.4.2 Mathematical Formulation

Simple filtration models have been presented by Herzig et al. (1970); Wnek et al. (1975); Dieulin (1982); Avogadro and de Marsily (1984); Avogadro (1984); and Champ and Schroeter (1988). In these models the reduction in colloid or solute concentration due to mechanical filtration is described by a filtration coefficient. For one dimensional fluid flow, with filtration and dispersion but without sorption the governing differential equations are modifications to (2.1) (Avogadro, 1984):

$$D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda v C = \frac{\partial C}{\partial t} \qquad (2.36)$$

and

$$\frac{\partial \sigma}{\partial t} = n \lambda v C \qquad (2.37)$$

where C = concentration of colloids in solution

σ = concentration of colloids fixed by filtration per volume of solid

λ = filtration coefficient

More complex models for filtration have been proposed including a distribution for the filtration coefficient (Avadadro and de Marsily, 1984), filtration with a Langmuir sorption reaction (Saltelli et al., 1985) and a comprehensive diffusion filtration and sedimentation model (Yao et al., 1971).

2.4.3 Discussion of Theory

The mathematical formulation presented in (2.36) and (2.37), if dispersion is neglected, would indicate that the profile of retained colloids (σ) should be a straight line on a semi-logarithmic plot with slope proportional to λ. Available laboratory experiments (Avogadro et al., 1981) for Am colloids however do not show this linearity and subsequent models (Avogadro, 1984) have used a log-uniform and log-normal distribution for the filtration coefficient and incorporated Langmuir sorption isotherms to obtain acceptable fits. The laboratory data also indicate that after saturation of the sorption sites, a small fraction of the input activity flows through the column with virtually no retention. This fraction may be accounted for by the smaller size microcolloids or by a soluble species.

The above experimental work has been performed on glauconite sands in the laboratory. There are almost no experimental results available for field tests of filtration in porous or fractured media. Champ (1988) and Champ and Schroeter (1988) describe the available data for porous and fractured media in Canada from work performed at the Chalk River Nuclear Laboratories, Ontario. Of particular interest are the particulate tracer experiments reported by Champ and Schroeter (1988) performed in a fractured monzonitic gneiss at a depth of 35 m. In these experiments the breakthrough curves for injected E-Coli bacteria and non-reactive particle tracers (polystyrene beads) were compared with those for conservative tracers. Rapid transport of a small percentage of the input concentration relative to conservative tracers for both bacteria and non-reactive particles was observed. The fact that various conservative tracers were used (^{3}H, Fluorescein, ^{82}Br, ^{32}P) would indicate that the accelerated breakthrough is most likely attributable to fewer flowpaths available to the particulate tracers (i.e., lower effective porosity). Removal of the bacteria and particles was

quantified through the calculation of filtration factors (λ) which were found to be in the range 0.2 to 0.54 m^{-1}, similar to those for a gravel aquifer. Filtration was a significant process in the particulate tracer tests in rock, as mass recoveries in the effluent averaged less than 5-10 percent of the total mass injected.

3. REVIEW OF TRACER TESTS

A review of the literature was performed to identify field and laboratory tracer tests for fractured crystalline rock that could be used to evaluate retardation parameters for use in subsequent generic nuclide migration modeling. Tracer tests of primary interest are those that used both conservative (non-sorbing) and sorbing tracers since this allows a more complete evaluation of different retardation mechanisms. In addition to reviewing the available literature, the research agencies associated with national radioactive waste management programs considering disposal in crystalline rocks, were contacted to obtain more up to date information. Countries contacted included, Britain, Canada, Switzerland and Sweden. The identified tracer tests are grouped according to laboratory and field tests.

3.1 LABORATORY TRACER TESTS

Only laboratory tracer tests on natural crystalline rock fractures were considered relevant to this review. Many of the earlier tracer migration experiments performed on crushed rock or polished rock coupons likely do not represent the sorptive behaviour of natural fractures. Table 3.1 summarizes the identified tests by core size, tracers, reference, test type, test duration and remarks. Seven groups of tests were identified. These tests were performed as part of the United States, Canadian and Swedish radioactive waste disposal programs on rock samples ranging from 0.02 to 1.0 m in size. Most tests utilized linear flow with either pulse, step or continuous injection of non-sorbing and sorbing tracers. Test durations ranged from a few hours to 2900 h (120 days). Strontium and cesium were the most commonly utilized sorbing tracers due to their relatively simple ion-exchange sorption and small, but measurable, retardation.

3.2 FIELD TRACER TESTS

Table 3.2 summarizes the identified field sorbing tracer tests performed in fractured crystalline rock. The tests are identified by site location, borehole spacing, tracers, reference, test type, test duration and

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Table 3.1 Summary of Laboratory Retardation Tracer Tests in Fractured Crystalline Rock

Test/Core Size	Tracers	Authors	Test Type	Test Duration (h)	Remarks
1) Stripa Granite 0.3 m core	NaLS, Sr^{2+}, Cs^{+}	Neretnieks et al. (1982)	- linear flow - pulse injection	90	- several tests, matrix diffusion inferred, linear isotherm
2) Lac du Bonnet 0.3 m block	^{3}H, ^{99}Tc, ^{75}Se, ^{137}Cs, colloids	Grondin et al. (1988) Grondin and Drew (1988)	- linear flow - continuous injection	2,900	- elution breakthrough curves for ^{3}H, ^{75}Se, ^{137}Cs, ^{99}Tc - autroadiography and selective extraction of sorbed species
3) Lac du Bonnet 1 m block	^{131}I, ^{137}Cs	Vandergraaf et al. (1988)	- linear flow - continuous injection	70	- supported by static sorption experiments
4) Stripa Granite 0.2 and 0.3 m core	^{3}H, NaLS, Br, I^{-} Sr^{2+}	Moreno et al. (1985)	- linear flow - continuous injection	2	- short duration experiments
5) Climax Granite 0.05 m cores	^{3}H, ^{85}Sr, ^{99}Tc, ^{137}Cs	Failor et al. (1982)	- linear flow - pulse injection	25	- only Cs retarded - small samples
6) Climax Granite 0.02 m cores	^{85}Sr, ^{137}Cs	Rundberg et al. (1982)	- linear flow - step injection	few hours	- small samples, no consecutive tracer tests
7) Miscellaneous Cores	^{3}H, ^{137}Cs, ^{235}Np ^{239}Pu, ^{152}Eu	Vandergraaf (1985) Eriksen (1983)	- linear flow	--	- difficult to interrupt

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Table 3.2 Summary of Field Retardation Tracer Tests in Fractured Crystalline Rock

Test/Borehole Spacing	Tracers	Authors	Test Type	Test Duration (h)	Remarks
1) Finnsjon Sweden - 30 m	I^-, Sr^{2+}, Cs^+ (non-radioactive)	Gustafsson and Klockars (1981); Hodgkinson and Lever (1983); Moreno et. al. (1983); Gustafsson and Klockars (1984)	- radial convergent - continuous injection	800	- good test INTRACOIN LEVEL 2 case - supported by lab sorption data
2) Studsvik Sweden (1978) - 25 & 51 m	^{82}Br, ^{85}Sr, ^{99}Tc, ^{75}Se, ^{113}Sn	Landstrom et al. (1978)	- radial convergent - pulse injection	1,300	- Tc not retarded; Sr moderately retarded; Se, Sn strongly retarded
3) Studsvik Sweden (1982) - 11.8 m	^{131}I, ^{3}H, ^{85}Sr, ^{134}Cs	Landstrom et al. (1982, 1983); Klockars et al. (1982)	- radial convergent - pulse injection	10,000	- Sr sorption data available, no Cs breakthrough
4) Chalk River (1984) - 10 m	^{82}Br, ^{85}Sr	Novakowski (unpublished)	- injection-withdrawal - pulse injection	350	- only rising side of Sr curve available
5) Ecoles des Mines - 12 m	Cl^-, I^-, Sr^{2+}, Cs^+	Calmels et al. (1979)	- radial convergent - pulse injection	10	- little retardation, high Q
6) Ecoles des Mines - 12 m	I^-, Cs^+, Sr^{2+}	Goblet et al. (1979)	- radial convergent - pulse injection	2	- little retardation, mostly significant tailing on curves
7) Chalk River (1985) - 12.7 & 29.8 m	^{82}Br, Fluoroscein, particulates	Champ and Schroeter (1988)	- radial convergent and injection-withdrawal - pulse injection	150	- filtration factor analysis for particulates (beads and E Coli)

remarks. Table 3.2 lists the seven major sorbing tracer tests that have been performed by French, Swedish and Canadian researchers studying radionuclide migration in crystalline rocks. The tests have been performed generally at shallow (<50 m) depths over distances of 10-30 m. Although the conditions under which these tests were conducted do not represent probable repository conditions (which are likely to be at depths of up to 1 km) these tests do represent the better controlled and well understood tests that are available. All tests include both sorbing and non-sorbing tracers. Typically strontium and cesium in both radioactive and nonradioactive forms have been used as sorbing tracers because of their relatively simple sorption behaviour and measurable retardation. Test durations ranged from 2 - 10,000 hours.

3.3 SELECTION OF TRACER TEST DATA FOR ANALYSIS

The identified sorbing tracer test data were reviewed to identify a data set for subsequent detailed analyses and parameter estimation. Parameters interpreted from this test are used in the prediction of radionuclide migration from a generic radioactive waste disposal site for periods of 10,000 years (Section 5). Because the long term radionuclide transport calculation will be made over temporal and spatial scales significantly greater than the laboratory and field scales of tests reported in Table 3.1 and 3.2, the following criteria, presented in order of relative importance, were used in selecting a set of sorptive tracer test data for detailed analysis and interpretation:

1) a large temporal and spatial scale;
2) complete non-sorbing and sorbing tracer effluent curves;
3) well-defined and simple groundwater flow path;
4) sorbing tracers with well defined sorption behaviour and measurable retardation;
5) supplemental testing (i.e., batch sorption tests, autoradiography).

Criterion 1 identifies field tracer tests as preferable over laboratory tracer tests and suggests the Finnsjon (1981), Studsvik (1978, 1982) and Chalk River (1984) tests as suitable for detailed analysis.

Criterion 2 eliminates the Chalk River (1984) tests as only the rising side of the Sr breakthrough curve was obtained. Criterion 2 also favours the Finnsjon tests over the Studsvik tests in that complete breakthrough curves were reported for Sr^{2+}, Cs^{+} and I^{-} for the Finnsjon tests. No ^{134}Cs breakthrough was reported for the Studsvik (1982) tests and only initial rising concentration curves were obtained for the ^{75}Se and ^{113}Sn migration in the Studsvik (1978) tests and for the laboratory ^{137}Cs tests of Grondin and Drew (1988).

Criterion 3 generally favours laboratory tests over field tests because of the more controlled conditions of laboratory tests. However, in view of the issue of sample representativeness in conjunction with the nature of the long term transport calculations, the importance of criteria 1 is greater than criteria 3 and field tracer tests are preferred. The characterization of the groundwater flow path is approximately equal for the Finnsjon and Studsvik tests. The injection withdrawal tests (i.e., Chalk River (1984), (1985)) are more difficult to interpret than the other radial convergent tests.

Criterion 4 indicates that tracer tests with sorbing tracers of Sr and Cs are preferred because of their relatively well understood sorption behaviour (Anderson and Allard, 1983) and measurable retardation.

Criterion 5 assesses the availability of supplemental testing, such as batch sorption tests, scanning of fracture surfaces using autoradiography to determine distribution of sorbed species, sectioning of rock to determine diffusion depths of sorbed species and selective chemical extractions to quantify sorption mechanisms. Criterion 5 favours laboratory tests over field tests. The supplemental data for laboratory tests are best for the Lac du Bonnet block tests and good for the Stripa granite core tests. Supplemental sorption experiments are available for the Finnsjon and Studsvik field tracer tests.

In consideration of the five criteria discussed above, the Finnsjon tracer test data were selected for more detailed study and parameter estimation. An additional benefit in using the Finnsjon data was that the I^{-} and Sr^{+2} data were selected as a test case for the INTRACOIN Level 2 model comparisons.

INTRACOIN is an international comparison effort set up to improve understanding of the various strategies for modeling radionuclide transport in geologic media (SKI, 1982). As a result, the I^- and Sr^{2+} data have been selected for such a comparison because they represent some of the better quality field data currently available.

4. INTERPRETATION OF FINNSJON TEST DATA

The Finnsjon tracer test data were interpreted using computer models that describe advection, dispersion and many of the retardation mechanisms described in Section 2 of this report. The test data were interpreted to provide a suite of parameters for use in performing long-term (10,000 year) radionuclide transport calculations. The following sections describe the Finnsjon tests, the approach used in analyzing the tracer test data, the numerical simulation models and the results of the simulations.

4.1 DESCRIPTION OF THE TESTS

The tests selected for analyses in this study are the two well, induced gradient I^- and Sr^{2+} tests conducted by Gustafsson and Klockars (1981; 1984) at the Finnsjon field research area as part of the Swedish high level radioactive waste disposal program. The Finnsjon research area is located about 140 km north of Stockholm in an area where the topography is relatively flat with ground elevations ranging between 20 and 44 m above sea level. Bedrock exposure at the site is quite high, averaging almost 20%. The bedrock consists of an older gneissic granodiorite and a younger granite.

The Finnsjon tracer tests were conducted at depths of approximately 90-100 m in a fracture that intersects boreholes G1 and G2 30 m apart. Two non-radioactive tracer tests were performed at this site, one with I^- and Sr^{2+} and one conducted later with I^- and Cs^+. The I^- and Sr^{2+} tests were selected for interpretation since they better fulfilled the criteria of Section 3.

The I^- and Sr^{2+} tracers were simultaneously injected into borehole G2 in a small (2 m) packed-off zone intersecting the fracture. Tracer was injected continuously into this zone for a period of 14.58 days at a constant flow rate of 2.7×10^{-7} m^3/s. The I^- tracer was injected as NaI at a concentration of 66.7 mol/m^3 (8465 mg/L) and the Sr^{2+} tracer was injected as $SrCl_2$ at a concentration of 94.7 mol/m^3 (8300 mg/L). Prior to tracer injection, a steady state flow system was established by pumping the injection and withdrawal wells for periods

of 2-3 days. Water was continuously removed from the entire borehole G1 at a rate of 1×10^{-4} m^3/s. Hodgkinson and Lever (1983) and Gustafsson and Klockars (1981) reported that the contribution of the fracture zone to this discharge from G1 is 2×10^{-5} m^3/s consequently a dilution of about 5:1 was introduced in the withdrawal borehole.

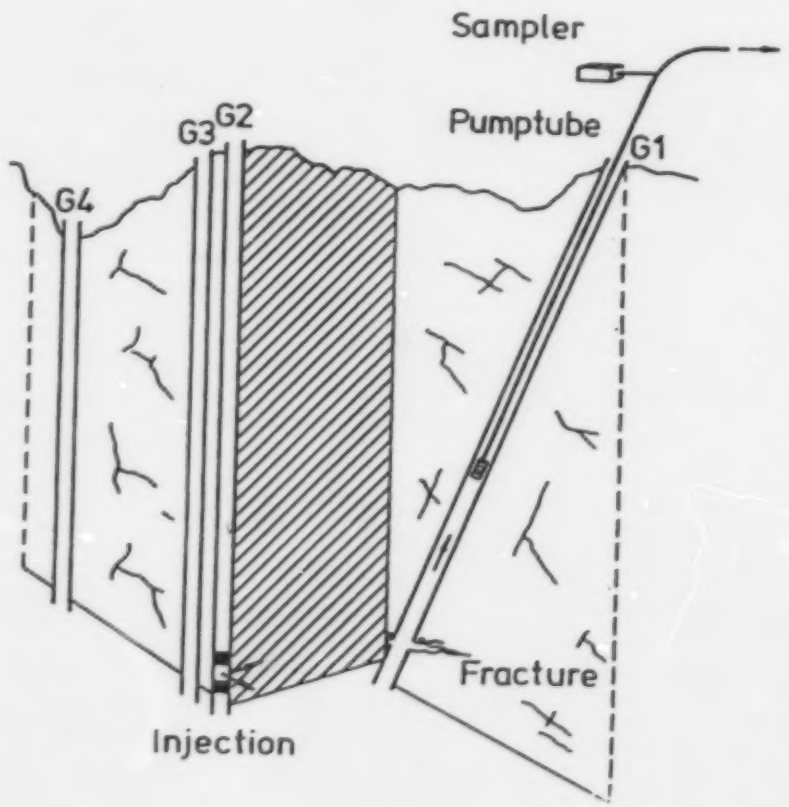
A schematic of the equipment setup of the test is shown in Figure 4.1. Table 4.1 presents a summary of the physical data describing the tests. Figure 4.2 shows the tracer injection flowrates and the breakthrough curves of I^- and Sr^{2+} expressed as C/C_o where C_o was the injection concentration. Figure 4.2 shows that Sr^{2+} was significantly sorbed but not significantly retarded relative to I^-. Mass recoveries of 98% and about 60% were observed for I^- and Sr^{2+}, respectively. No other geochemical data describing the withdrawal water was reported during the test or the pre-injection pumping.

4.2 APPROACH

The advection dispersion equation presented in Equation (2.1) contains two parameters that describe physical properties of the media. These parameters, interstitial velocity and dispersivity, can only be evaluated through the use of a conservative tracer. Dispersivity represents the spatial variation in velocity that exists in a medium (e.g., fracture zone) and is caused by the existence of various interconnected pathways as well as the variation in velocity across a particular fracture. The interstitial velocity differs from the Darcy velocity (i.e., flux per unit area) since the former provides an estimate of the linear groundwater velocity. The two quantities are related through an effective porosity which considers only the active porosity within the flow zone.

The approach followed in the interpretation of the Finnsjon test data for the purpose of evaluating retardation mechanisms and providing parameters for subsequent long-term radionuclide migration calculations was as follows:

1) Use the non-sorbing tracer (I^-) data to determine physical parameters of the Finnsjon test (e.g., interstitial porosity and dispersivity);



Drawn by	Date	LAYOUT OF FINNSJON TRACER TEST SITE (FROM HODGKINSON AND LEVER, 1983)
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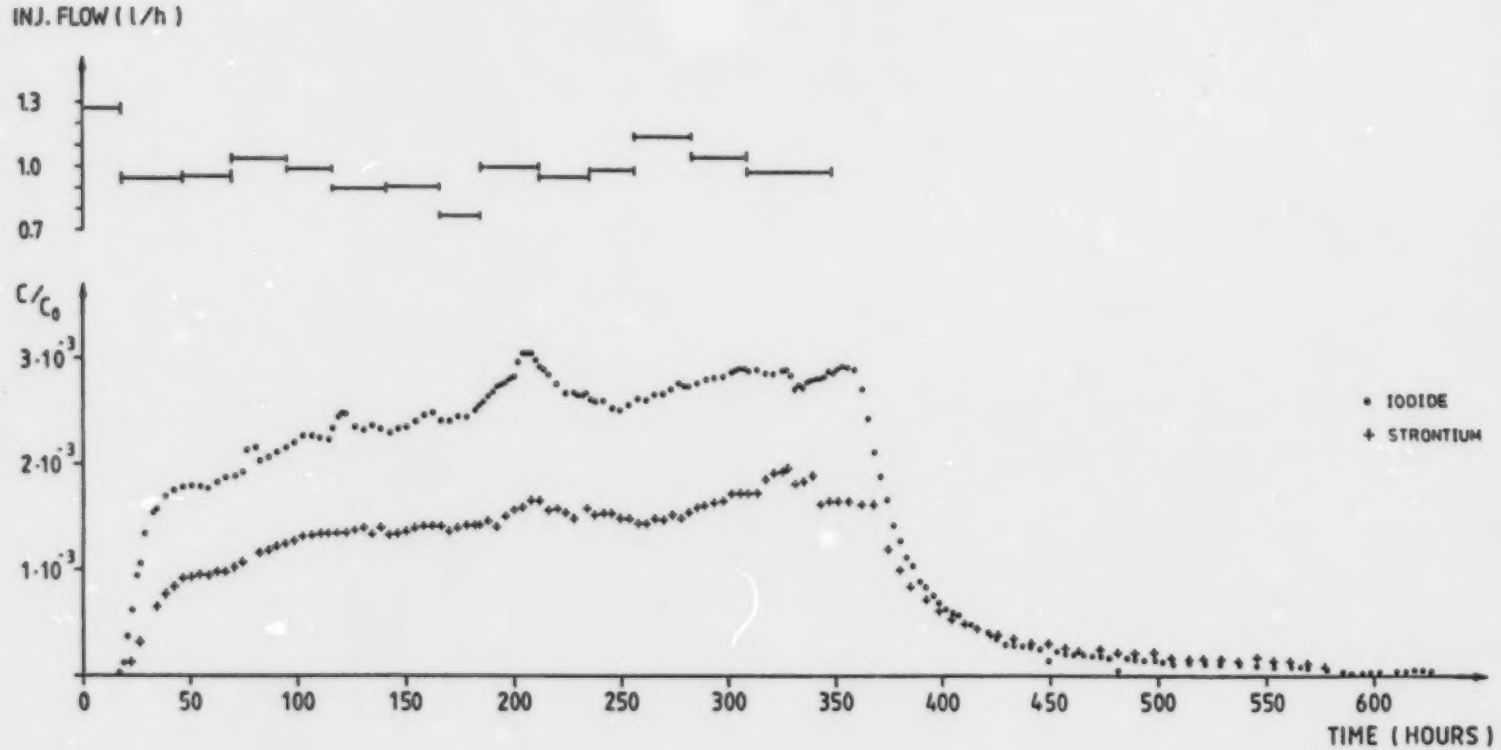
INTERA Technologies		FIGURE 4.1

Table 4.1 Physical Parameters of the Finnsjon I^- and Sr^{2+} Tracer Tests

Parameter	Value
Radius of measurement borehole	0.11 m
Radius of injection borehole	0.11 m
Distance between boreholes	30.0 m
Pumping rate in measurement borehole	1.0×10^{-4} m^3/s
Discharge rate from fracture	2.0×10^{-5} m^3/s
Mixing length in measurement borehole	100.0 m
Period of injection	1.26×10^{6} s
Injection rate (I^-)	1.8×10^{-5} mol/s
Injection rate (Sr^{2+})	2.5×10^{-5} mol/s



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INJECTION FLOWRATES AND I^- AND SR^{2+} BREAKTHROUGH CURVES - FINNSJON TRACER TESTS (AFTER GUSTAFSSON AND KLOCKARS, 1984)

FIGURE 4.2

2) Interpret the sorbing tracer (Sr^{2+}) data by using the same physical parameters as interpreted from the non-sorbing test while calibrating to a single retardation mechanism.

In adopting this approach we have made the assumption that anion exclusion and anion exchange are not significant factors in I^- migration. While this may or may not be correct it is necessary to make this assumption in order to determine an interstitial velocity.

In following the above approach, both physical and retardation parameters were determined by visually fitting the simulations of a numerical model to the tracer breakthrough curves shown in Figure 4.2. Numerical models were selected because of their greater flexibility over analytical or semi-analytical solutions to the governing differential equations described in Section 2 of this report. General descriptions of the numerical models and the conceptual model of the fracture/rock system tested at Finnsjon are provided in Section 4.3.

Visual fitting of the numerical model results to the field data is an appropriate method for evaluating parameter values given the uncertainty in the flow field and transport mechanisms in the Finnsjon tests and the general objectives in this study.

In evaluating parameter values determined from the interpretation of the tracer test data, we have considered the degree to which the model parameters are representative of parameter values determined from other field and laboratory testing. Physically unrealistic parameter values which may provide reasonable fits to parts of the tracer breakthrough curves were not used in this study. For example, unrealistically high dispersivities of 30 - 300 m can provide a reasonable fit to parts of the I^- breakthrough curve. However this dispersivity in the context of the inter-borehole travel distance indicates a Peclet number (Pe) of 1.0 - 0.1 which is approximately one to two orders of magnitude less than other reported Pe for transport in fractures (Neretnieks, 1985).

The Sr^{2+} breakthrough data were evaluated in the context of the retardation mechanisms identified in Section 2 and the physical characteristics of the fracture/rock flow system determined from analysis of I^- tracer test. Because the choice of simulation model is highly dependent on the type of retardation mechanism being considered a brief discussion of the relevance of the major retardation mechanisms discussed in Section 2 to the Finnsjon test data is provided the following sections.

4.2.1 Precipitation - Coprecipitation/Dissolution

Precipitation - coprecipitation/dissolution is a potentially significant mechanism in the Finnsjon Sr^{2+} tracer test. Gustafsson and Klockars (1984) have reported that some form of irreversible reaction with the medium (e.g., precipitation) was necessary to explain the low mass recoveries of the Sr^{2+} tracer. Gustafsson and Klockars calculated, using thermodynamic models and available groundwater and tracer chemistry data, that the amount of Sr^{2+} lost through precipitation of $SrCO_3$ and $SrSO_4$ was at most only 6% and therefore other unknown irreversible reaction mechanisms were responsible for the loss of 34% of Sr^{2+}. Other investigators (Hodgkinson and Lever, 1983; Moreno et al., 1983) have assumed a simple Sr^{2+} removal mechanism to account for the lower mass recoveries. Given the uncertainty in the type of irreversible reactions, we have assumed a removal mechanism expressed as a reduction in source concentration to account for the low mass recoveries. This implies a negligible effect on retardation of Sr^{2+} as is evident in the Sr^{2+} breakthrough curves.

4.2.2 Sorption

The breakthrough curves of Sr^{2+} show a small amount of retardation relative to I^- which may be accounted for by a sorption mechanism as described in Section 2 of this study. As indicated in Section 2, it is generally not possible in most experimentation to isolate the different sorption mechanisms such as physical, electrostatic and specific adsorption because all sorption mechanisms are usually described using similar expressions, such as isotherm models or multiple parameter sorption models. In our analysis of sorption

behaviour we have followed other investigators (Landstrom et al., 1982; McKinley and West, 1982; Moreno et al., 1983; Hodgkinson and Lever, 1983) and have considered simple linear and Freundlich isotherms both with kinetic effects to characterize sorption processes in the fracture/matrix system at the Finnsjon site.

4.2.3 Diffusion

Diffusional retardation processes are significant for the interpretation of both the I^- and Sr^{2+} breakthrough curves. Moreno et al. (1983) and Hodgkinson and Lever (1983) have reported that diffusional processes are necessary to simulate the shape of the Finnsjon tracer tests curves. Characterization of diffusion processes are important for the long-term radionuclide transport calculations because quantification of the volume of matrix pore space available for diffusion has direct impact on the resultant breakthrough curves. Different geometries for diffusion and different types of diffusion (matrix, immobile fluid zones, surface diffusion) can be considered but distinction between the different geometries and types is generally not possible in the interpretation of the tracer tests. In our analyses of the Finnsjon tracer tests, the diffusional loss/gain of solute is modeled under different geometries because plane parallel plate flow (as a slab geometry) and channelled flow (as a radial geometry) are likely bounding cases for flow regimes in large, high permeability fractures such as the one tested at Finnsjon.

4.2.4 Filtration

Colloidal transport and therefore filtration effects are not likely to be significant for the Sr^{2+} tracer tests at Finnsjon because of the high concentrations of Sr^{2+} used in the test and the shape of the Sr^{2+} breakthrough curves. Filtration as a removal or retardation mechanism can only be important in the Finnsjon test if organic complexes, micro-organisms or other colloidal matter exists at concentrations that approximate the effluent concentrations of the Sr^{2+}. Avogadro (1984) and McKinley et al. (1986) reported that natural colloid and micro-organism contents in granite groundwaters are usually less than

1 mg/L. If all of these colloidal and micro-organisms were capable of complexing or carrying Sr^{2+} the maximum amount of filtration would be 1 mg/L. Because the influent and effluent Sr^{2+} concentrations were 8300 mg/L and up to 16 mg/L respectively, filtration will not be significant retardation mechanism in the Finnsjon Sr^{2+} test.

4.3 MODEL DESCRIPTIONS

Two numerical models (SWIFT II and HCTM) were used to analyze the Finnsjon I^- and Sr^{2+} tracer breakthrough curves shown in 4.2.

The SWIFT II model (Sandia Waste-Isolation Flow and Transport Model for Fractured Media; Reeves et al., 1986) was utilized to simulate conservative solute behaviour and most of the retardation mechanisms evaluated in this study.

The SWIFT II model is a finite difference model that solves the partial differential equations describing flow and transport of a contaminant in a dual porosity system for a variety of geometries for both the matrix and fracture. The SWIFT II model can consider the following general retardation mechanisms as described in Section 2 of this report.

- Sorption within the fracture may be modeled as a Freundlich or linear (Kd) isotherm;
- Sorption within the matrix may be modeled as a linear (Kd) isotherm;
- Diffusion from the fracture to the matrix or to an immobile porosity may be modeled considering slab or radial geometries of the matrix (i.e., diffusion from a parallel plate fracture or from a high permeability narrow channel).

The HCTM model (Hydrology Contaminant Transport Model; INTERA, 1982) was also used to simulate the migration of sorbing solute. HCTM is also a finite difference model that solves the partial differential equations describing flow and transport of a contaminant in a porous medium. HCTM was used to model simple first-order kinetic sorption and desorption effects as described by equations (2.18) and (2.19).

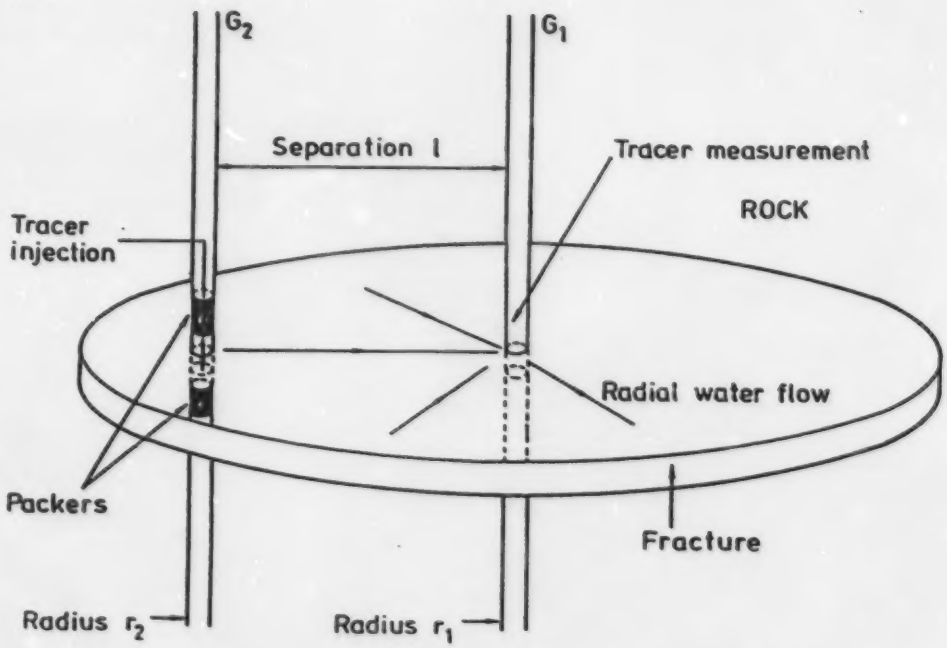
The Finnsjon tracer tests were performed under approximate radial convergent flow conditions as conceptually illustrated in Figure 4.3. The radial convergent flow field approximation was valid because a relatively small flowrate of water (2.7×10^{-7} m^3/s), equal to about 1-2% of the withdrawal flowrate from the fracture, was injected with tracers at borehole G2. To simulate the physical system conceptually illustrated in Figure 4.3, a radial mesh comprising 60 grid blocks was used. Typically simulations performed in this study were carried out using a sufficient number of time steps (approximately 1000) to ensure an accurate numerical solution (i.e., minimize numerical dispersion and/or overshoot-undershoot problems).

4.4 RESULTS

The following sections describe the results of the model simulations for the iodine and strontium tracers. In all figures showing model simulations and field data, the field data are plotted with asterisks and the model simulations are plotted as a smooth line.

4.4.1 Iodide

The philosophy followed in analyzing this tracer test (as well as all other tests) was to initially try to reproduce the observed data using the fewest number of mechanisms as possible. In the case of I^-, we first attempted to match the breakthrough curve using only longitudinal dispersivity and travel time between the boreholes. Because of the one-dimensional geometry of the model, transverse dispersivities are unimportant. Travel time for this steady state flow field is governed by the fracture flow rate (flux) and the fracture aperture



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CONCEPTUAL MODEL OF THE FINNSJON TRACER TESTS

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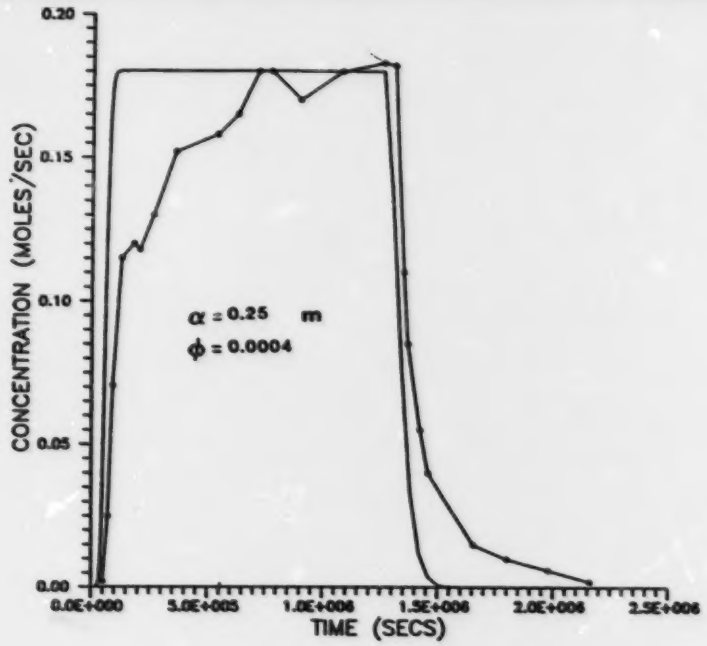
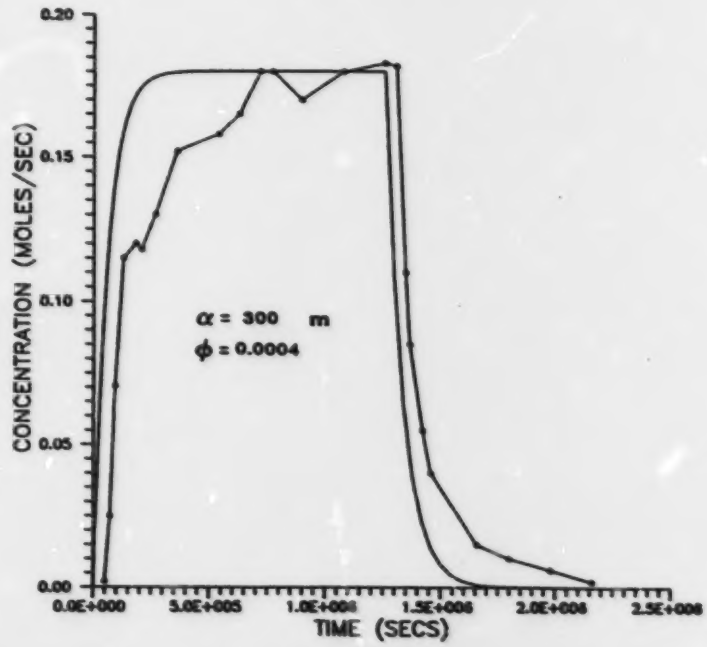
FIGURE 4.3

which, in a dual porosity formulation, will be represented by the interstitial porosity. Hodgkinson and Lever (1983) reported a value of 410 um for this parameter and, as an initial estimate for our unit thickness fracture, we selected interstitial porosity to correspond to this quantity by setting it equal to 0.0004.

Figure 4.4 presents the results of two bounding simulations in which the porosity was set to 0.0004 and dispersivity was varied from 0.25 m to 300 m. It can be seen that the higher dispersivity simulations better represent the overall shape of the observed curved (by rounding sharp corners and creating a more significant tailing effect). However the initial breakthrough from the model occurs virtually at the same time that the tracer is injected at borehole G-2 located 30 m from the withdrawal borehole. This is physically unrealistic. Furthermore, even at the highest dispersivity used, this smoothing is not sufficient to replicate the observed data.

Another discrepancy between simulated and observed data for porosity of 0.0004 and dispersivity of both 0.25 and 300 m is the relative position of the two curves. The fact that simulated rising and falling limbs occur slightly ahead of the observed limbs implies that a slower water travel time is required in the model. Two additional simulations were conducted to examine the effect of travel time. These simulations used an interstitial porosity of 0.001 and dispersivities of 0.25 and 300 m (Figure 4.5). Plots of both sets of modeled data demonstrate a noticeable shift to the right (relative to porosity of 0.0004) reflecting the decreased interstitial initial velocity. For the lower dispersivity case, the higher porosity produces what could be called an inferior match since the rising and falling limbs lag the observed and the initial breakthrough point is poorly reproduced. For the higher dispersivity case the fit, at first glance, appears acceptable, even quite good. However, the instantaneous breakthrough of tracer indicated by the model and caused by the high dispersivity and low Peclet number (0.1) are physically unrealistic. Minimum Peclet numbers for transport in single fractures over similar distances have been reported by Neretnieks (1985) and Raven et al. (1989) as about 5 - 15. From this modeling we concluded that simple advection - dispersion models could not adequately reproduce the observed I^- breakthrough curve.





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CALCULATED AND OBSERVED I^- BREAKTHROUGH CURVES FOR ϕ = .0004 AND VARIOUS α

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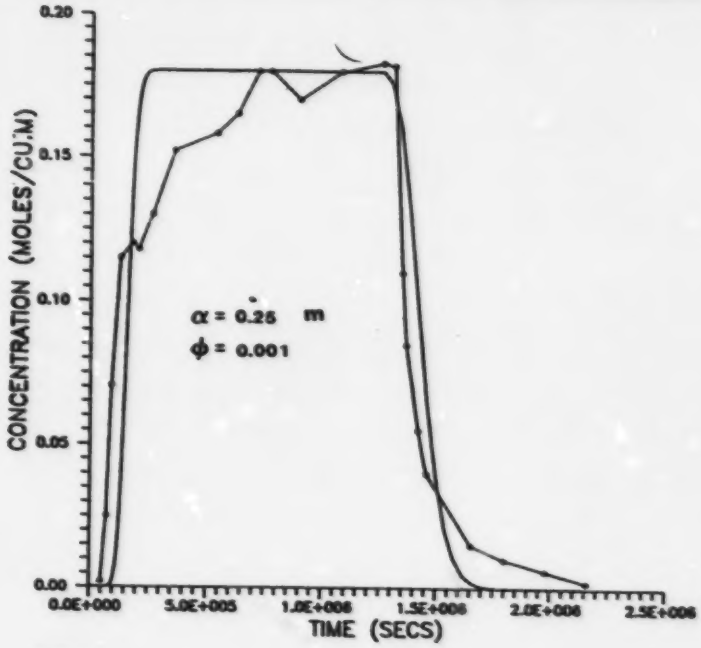
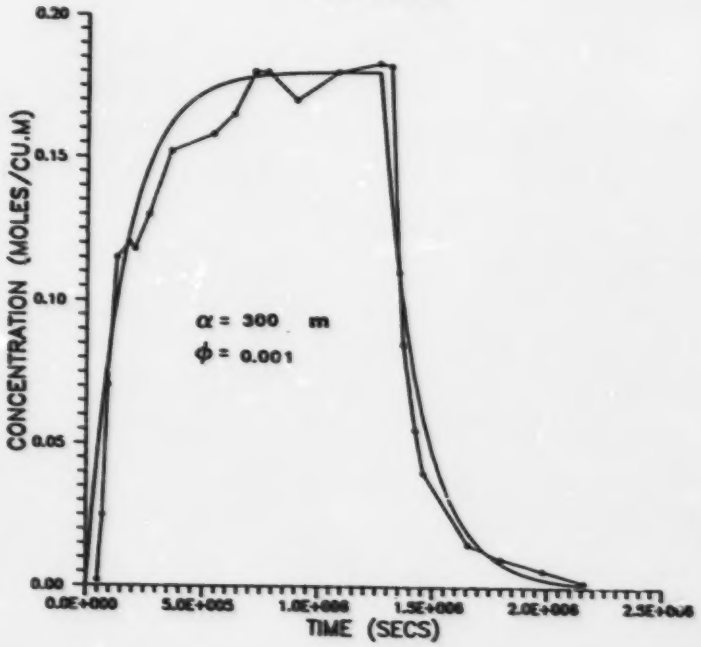
FIGURE 4.4





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CALCULATED AND OBSERVED I^- BREAKTHROUGH CURVES FOR ϕ = .001 AND VARIOUS α

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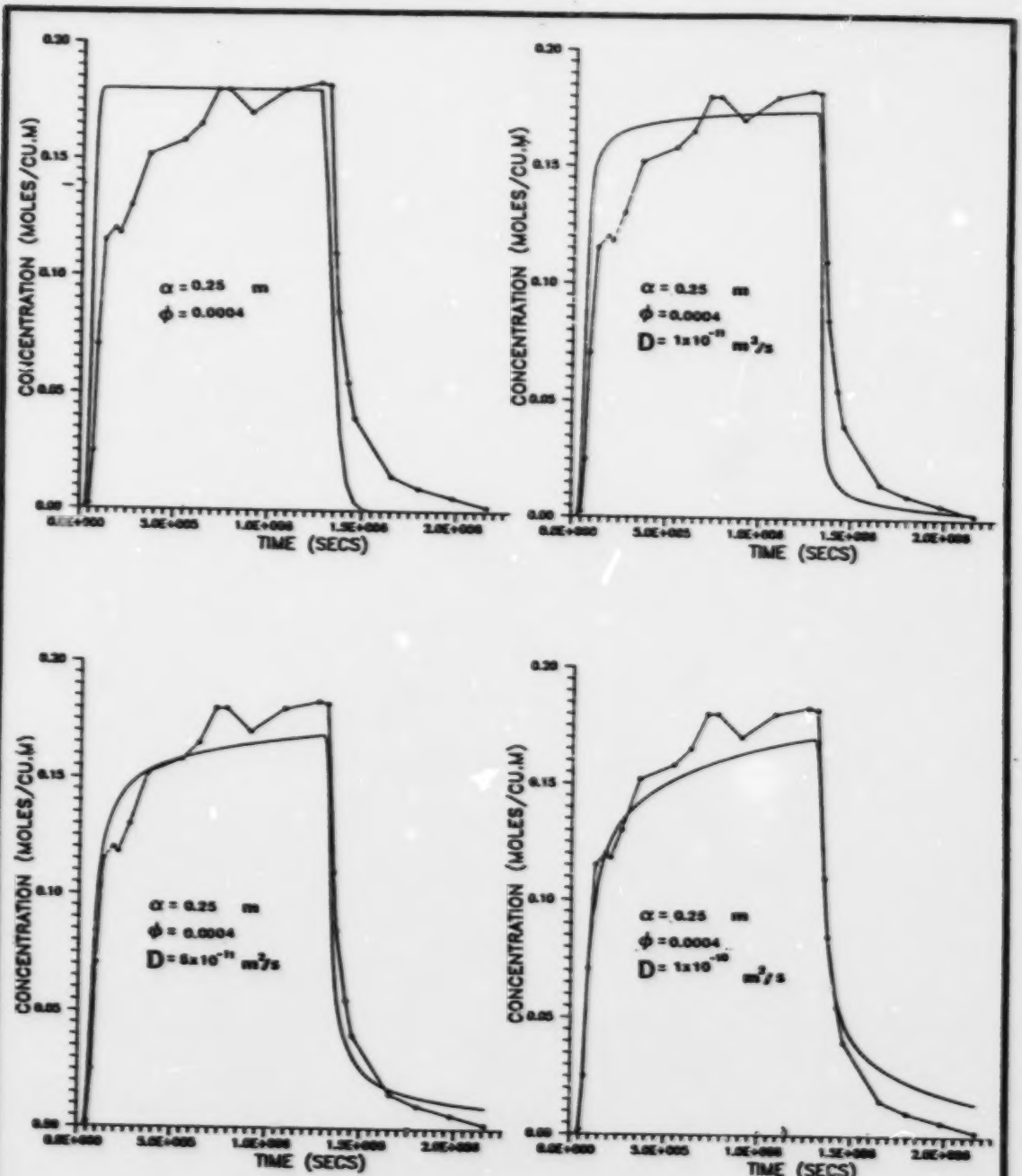
FIGURE 4.5

The next set of simulations were slightly more sophisticated in that they included the effect of matrix diffusion. The model has the capability of assuming either a planar or radial geometry to represent the diffusion of tracer into the matrix. The first geometry selected was a planar (or slab) geometry in which the matrix was assumed to exist above and below the fracture zone. A sufficiently thick matrix was assumed to ensure that the matrix would not be exhausted during the simulation. The physical parameters selected for these simulations were matrix porosity of 0.005 interstitial porosity of 0.0004 and dispersivity of 0.25 m. These base case parameters were selected because they better simulate the early part of the I^- breakthrough curve which experience has shown would only be marginally influenced by matrix diffusion effects. Matrix diffusion effects will more strongly influence the later parts of the breakthrough curve resulting in a slower rise in tracer concentration and more extensive tailing. Figure 4.6 shows the results of these simulations for effective diffusion coefficients of 1×10^{-10}, 5×10^{-11} and 1×10^{-11} m^2/s. Also shown, for comparative purposes, is the base case simulation with no matrix diffusion. The effect of matrix diffusion can be evaluated by comparing the different breakthrough curves. Some of these effects include a lowering of peak concentrations and the creation of a tailing behaviour, both of which are proportional to the magnitude of the diffusivity. For the planar or slab matrix geometry an effective diffusion coefficient of 5×10^{-11} m^2/s gave a good fit to the I^- breakthrough curve.

Figure 4.7 presents the results of two additional simulations in which the geometry of the matrix diffusion was changed from slab to radial. A radial geometry is more representative of a diffusion from a high permeability channel or streamtube (Rasmuson and Neretnieks, 1986). Also shown, for comparative purposes, is the "best fit" breakthrough curve for the planar geometry. The first radial matrix geometry simulation used the same diffusivity as determined from the slab geometry simulations. The simulated results for this case are significantly different from those of the slab geometry and are indicative of greater mass exchange between the fracture and matrix. A lower diffusivity of 1×10^{-11} m^2/s yields an acceptable fit for the radial configuration (see Figure 4.6). The increase mass exchange is expected as the concentration gradients and therefore mass flux are greater for a radial geometry than for a slab geometry.



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EFFECT OF MATRIX DIFFUSION ON I⁻ BREAKTHROUGH CURVE

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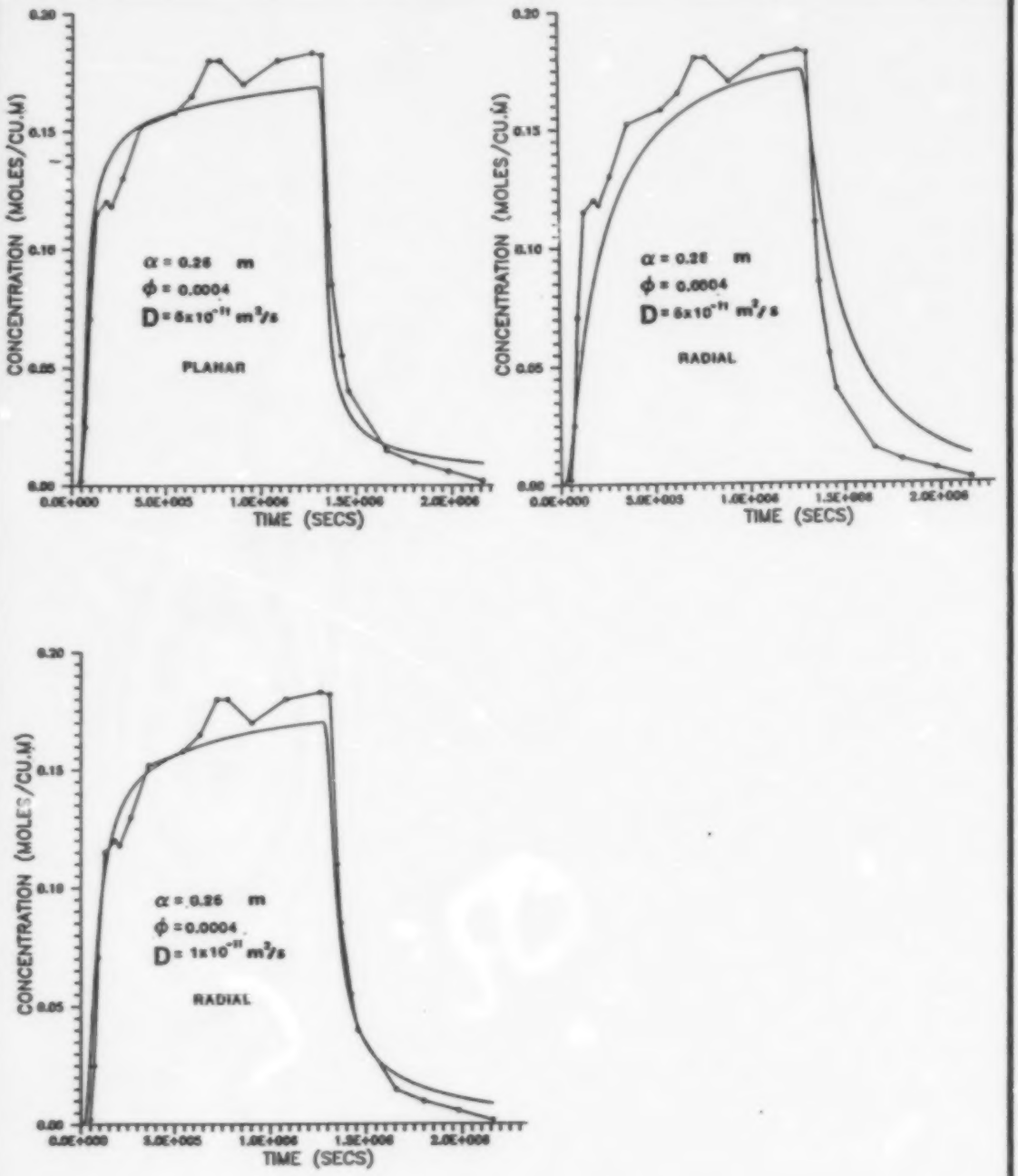
FIGURE 4.6



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SENSITIVITY OF I^- BREAKTHROUGH CURVE TO MATRIX GEOMETRY

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FIGURE 4.7

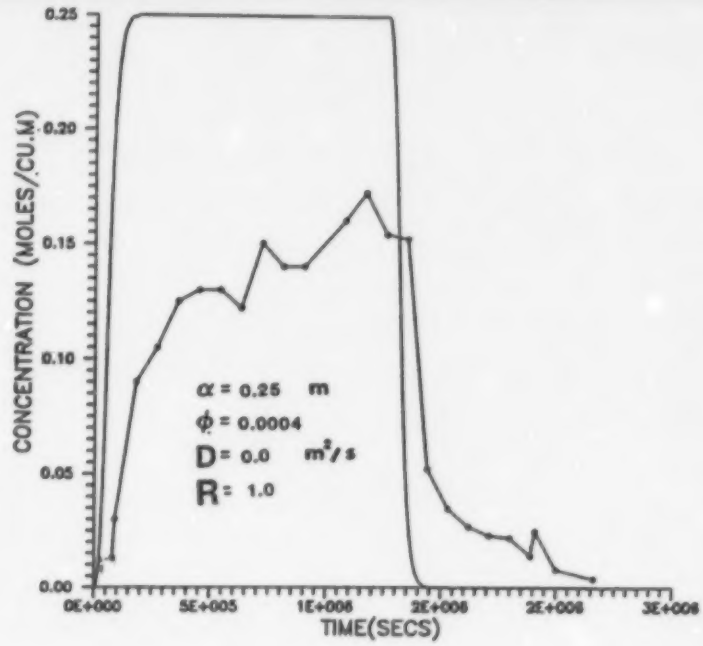
Changes in matrix geometry from slab to radial or cylindrical result in offsetting or compensating retardation phenomena, not all of which can be considered by the models used in this study. For example, flow in high permeability channels likely increases the concentration of solute in the channel and reduces the area available for diffusion as a result of active flow occurring on only a small percentage of the total fracture surface. The first of these effects results in higher mass fluxes, the second results in lower mass fluxes. The net effect of changes in geometry is likely to increase the mass flux rate between the fracture and matrix.

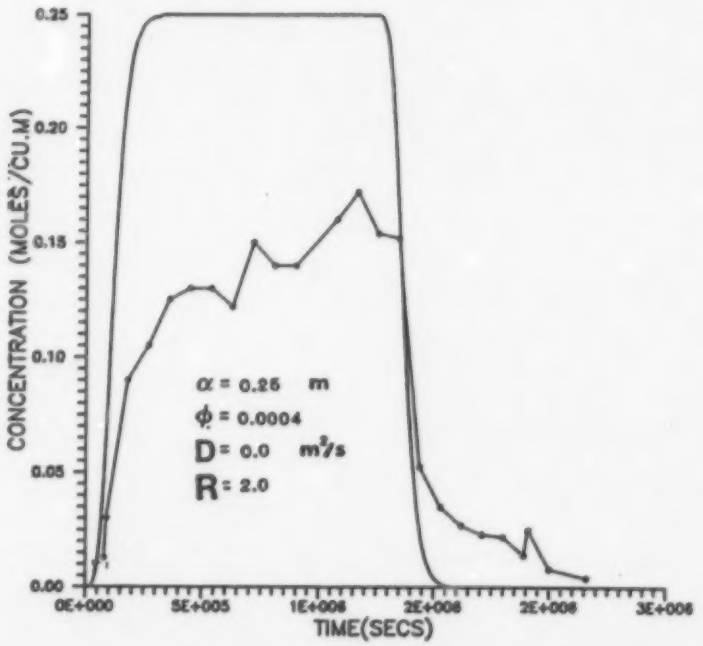
The values of matrix diffusion coefficient derived from our modeling of the I^- data are about two to three orders of magnitude greater than laboratory experiments and generally consistent with diffusion coefficients interpreted by Moreno et al. (1983) (2×10^{-10} m^2/s) and Hodgkinson and Lever (1983) (about 4×10^{-11} m^2/s) using similar models. The high diffusion coefficients suggest that diffusional exchange between mobile and immobile/zones within the fracture plane may be important for the Finnsjon tests or that enhanced diffusion exists on the weathered surfaces of the fractures.

4.4.2 Strontium

The model simulations conducted for Sr used the same conceptual (and numerical) model that was previously used for I^-. The first simulation consisted of merely injecting the full amount of tracer and assuming no retardation or matrix diffusion was operable. The interstitial porosity and dispersivity used in these simulations correspond to best fit iodide values of 0.0004 and 0.25 m. These parameters represent physical characteristics of the system and consequently should not change as a function of tracer. The results of the first Sr^{2+} simulation are presented in Figure 4.8. The most significant observations that can be made regarding this breakthrough curve include:

1. The significantly higher magnitude of the peak concentration of the simulation;
2. The more rapid breakthrough of the unretarded simulated front;





Drawn by	Date	EFFECT OF SORPTION BASED RETARDATION (R) ON SR^{2+} BREAKTHROUGH CURVE	
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INTERA Technologies			FIGURE 4.8

3. The "less dispersed" shape of the simulated curve.

Observation 1 reflects the poor recovery of Sr^{2+} likely attributable to some irreversible reactions with the medium, while observation 2 indicates that some form of retardation is likely operational. The "less dispersed" shape of the simulated curve can be seen by comparing rising and falling limbs of the two curves. Although we have used the term "less-dispersed", we do not imply that the Sr^{2+} behaviour is attributable to dispersion. It is much more likely that this behaviour is due to whatever removal mechanism is causing the peak attenuation. In order to examine the significance of sorption-based retardation, we performed a simulation in which a relatively weak sorption isotherm was assumed to govern Sr^{2+} behaviour. The isotherm chosen initially corresponded to a linear ($Kd = 1.6 \times 10^{-7}$ m^3/kg) isotherm which yields a retardation factor of approximately two. The results of this simulation are also presented in Figure 4.8. It can be seen that the only significant effect that this sorption behaviour has on the breakthrough curve is to lag the entire curve. It should also be noted that a retardation factor of two is sufficient to yield a reasonable match (from a time lag behaviour standpoint) with the observed data. While the observations associated with sorption based retardation may be intuitively obvious the implications associated with these observations are less obvious. For example based on this observation it is possible to infer:

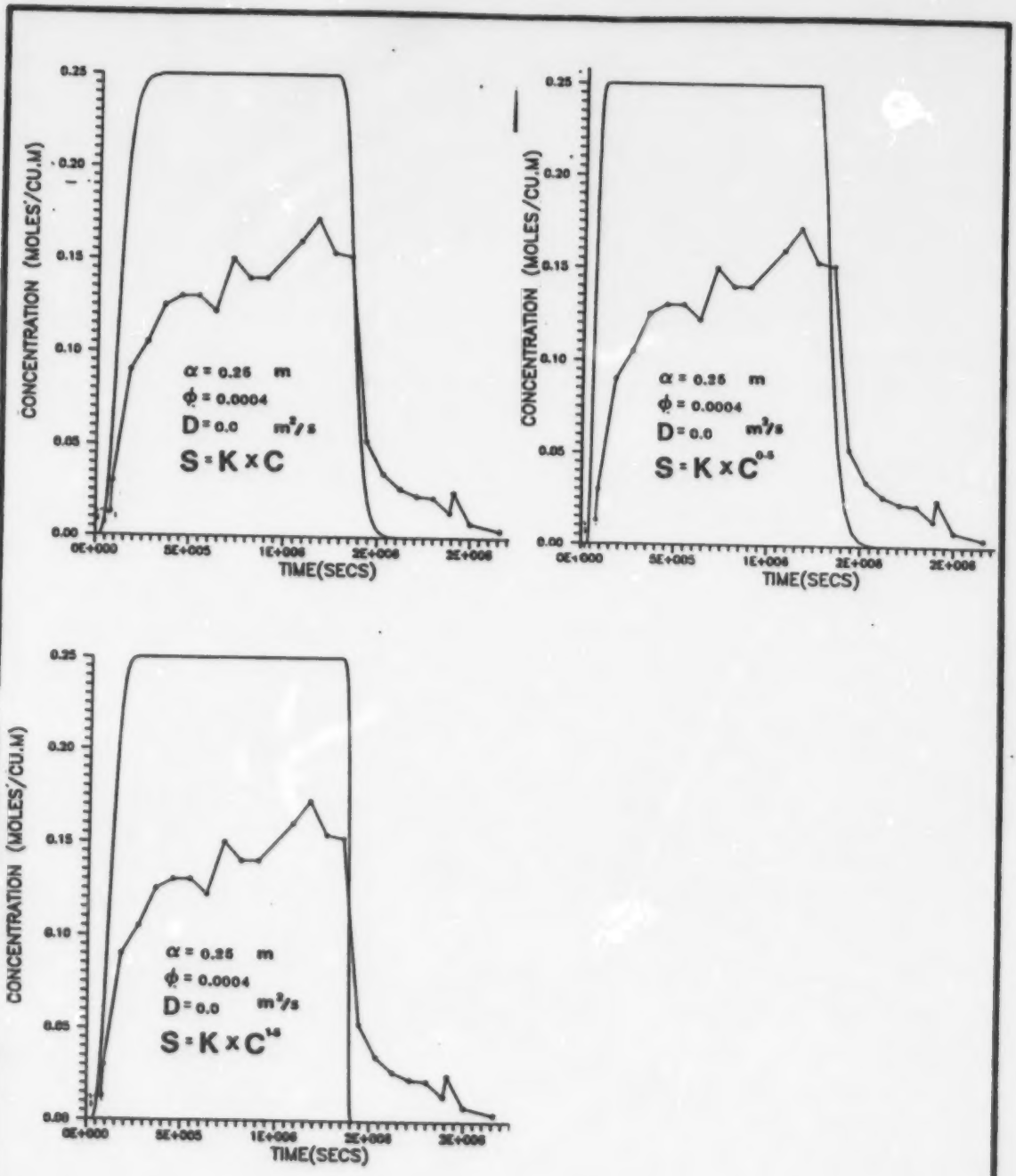
1. Kinetic behaviour is unlikely to be significant;
2. Other sorption isotherms are unlikely to produce significantly different results.

Inference 1 is based on the fact that kinetic sorption behaviour represents the time required for sorption to reach equilibrium. The two bounding cases for this condition correspond to a time of zero (which represents the equilibrium sorption case) and a time of infinity (which represents the zero sorption, i.e., unretarded case). Consequently, the inclusion of kinetic behaviour will result in breakthrough curves that are between the unretarded and

the retarded curves presented in Figure 4.8. Although not shown in this report, HCTM modeling of the Sr^{2+} breakthrough curves considering various sorption and desorption rate constants showed behaviour bounded by the two cases described above.

Retardation due to sorption is a relatively minor process as evidenced by the small difference between the retarded and unretarded curves. Consequently little can be gained by using alternate isotherm relations. To verify this latter hypothesis two simulations were performed in which a Freundlich isotherm was used. The first of these simulations used an exponent (N) of 0.5 and left the coefficient (K) of the isotherm equal to the original Kd value of 1.6×10^{-7} m^3/kg. The second simulation used an exponent of 1.5. The coefficient for this isotherm was reduced by slightly over one order of magnitude. The reason for this change was to allow the breakthrough to occur at approximately the same point in time. This was necessary because an exponent of 1.5 will cause significantly greater sorption to occur. To compensate for this additional retardation the coefficient must be reduced. The results of these simulations are presented in Figure 4.9. Although slightly better fits could be obtained by refining the isotherm coefficient these curves have been presented merely to demonstrate the effect of using a Freundlich isotherm to represent sorption. Also presented is the breakthrough curve corresponding to a linear (Kd) isotherm. It can be seen that little difference exists between the three curves. The lag time differences could be eliminated by further calibration of the isotherm coefficient. The only difference between the curves is a slight smoothing (or flattening) of the rising limb of the curve and a sharpening of the downlimb portion for increasing exponent values. Similar behaviour has been reported by other investigators (Van Genuchten and Cleary, 1979). Unfortunately, because sorption does not play a more significant role, the difference between the three curves is negligible.

The next set of simulations that were conducted examined the effect of matrix diffusion without considering sorption. The first simulation used the same diffusion coefficient determined from the best fit of the iodide tracer test (i.e., 5×10^{-11} m^2/s) considering slab or geometry. All other physical



Drawn by	Date	COMPARISON OF LINEAR AND FREUNDLICH ADSORPTION ISOTHERMS FOR SR^{2+} BREAKTHROUGH CURVE
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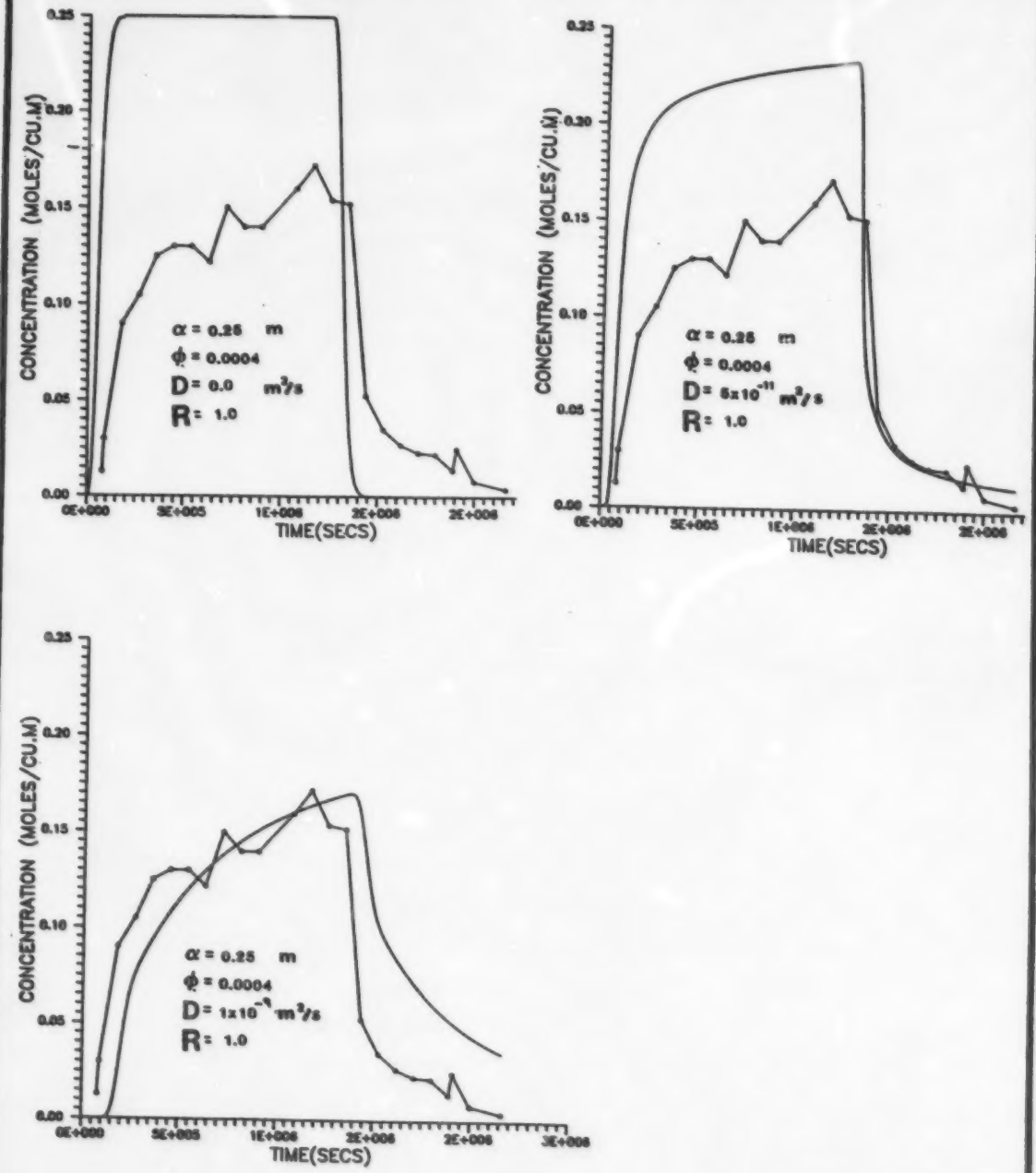
parameters the same as for the iodide test. The results of this simulation are presented in Figure 4.10. Also presented is the breakthrough curve corresponding to a non-sorbing non-diffusing species. By comparing the two curves to the observed concentration breakthrough it can be seen that both simulated curves arrive ahead of the observed curve. Furthermore, both curves have peaks that are substantially higher than the observed values. The shape of the curve corresponding to a matrix diffusion coefficient of 5×10^{-11} m^2/s more closely resembles the observed data although it must be pointed out that neither curve is capable of reproducing the observed curve with acceptable accuracy. From a close examination of Figure 4.10, it is apparent that matrix diffusion may cause a reduction in the peak concentrations of the breakthrough curve as well as causing a slight retardation of the entire curve. To examine whether matrix diffusion by itself could explain the apparent loss of tracer a third simulation, also presented in Figure 4.10, was undertaken. This simulation uses a value of 1×10^{-9} m^2/s for a diffusion coefficient. This value is comparable to free water diffusion coefficients and is too high to be representative of diffusion in a rock matrix. It may be argued that such high diffusivities are indicative of diffusion into immobile fluid zones. The breakthrough curve representing this simulation exhibits a poor fit to the observed data. Although peak concentrations are much more consistent with observed values, the curve exhibits too much retardation due to matrix diffusion. In addition, the "tailing" behaviour is too pronounced when compared to the observed data. If the iodide tracer did not exist it might be possible to obtain a significantly improved fit by decreasing the interstitial velocity of the fracture zone. However, doing this would cause an inconsistency with known data for the Finnsjon test.

The last set of simulations attempted to improve the fit between calculated and observed breakthrough curves by assuming a removal mechanism (such as irreversible precipitation or co-precipitation). The easiest way of incorporating these effects into the tracer test simulations is through reduction in the source term. Hence for these simulations the input concentration was reduced by a constant factor. It is recognized that this is a simplistic, and



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IMPACT OF MATRIX DIFFUSION ON SR^{2+} BREAKTHROUGH CURVES

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FIGURE 4.10

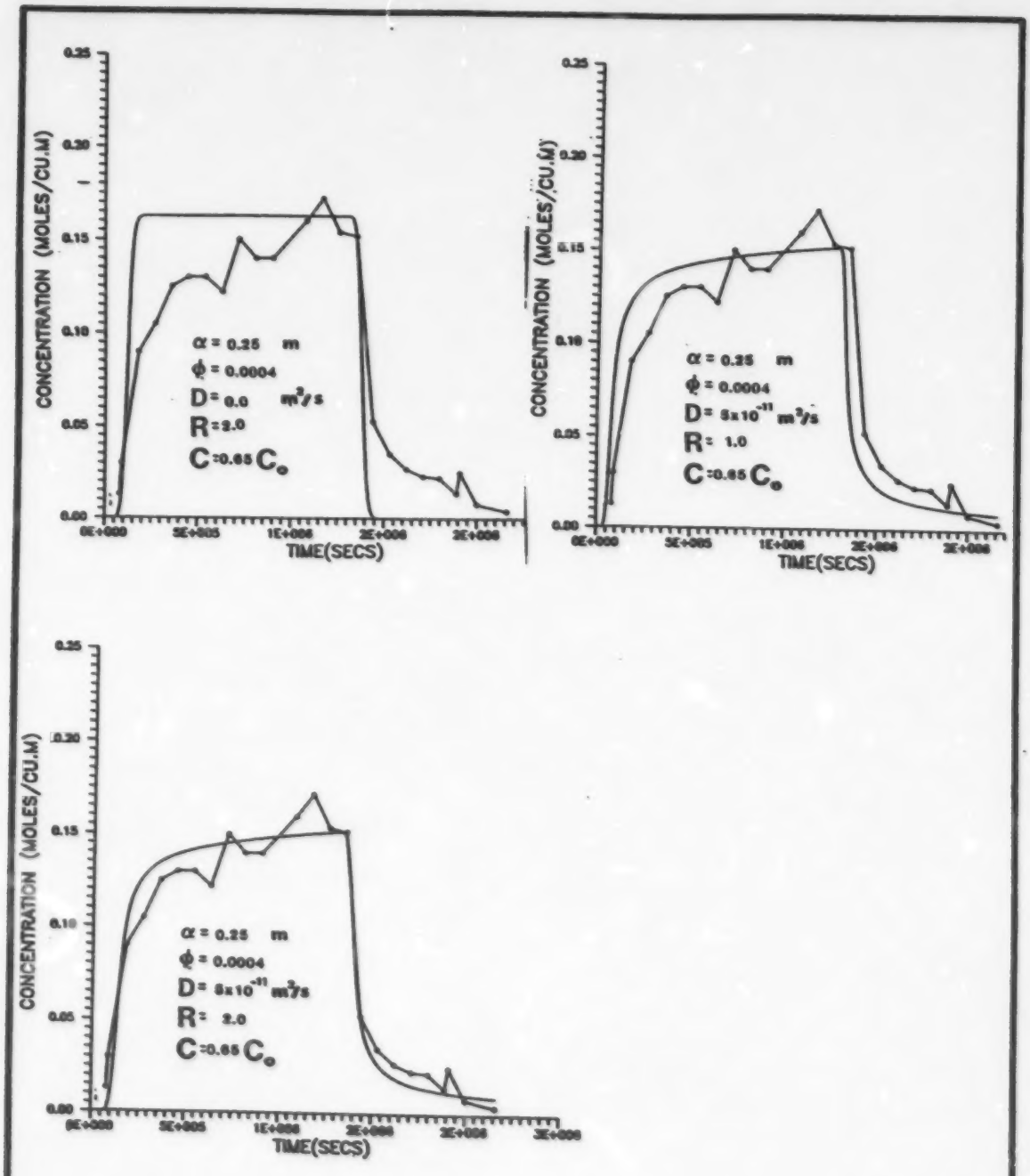
possibly erroneous, way of incorporating irreversible precipitation reactions. However in view of the level of detail available describing geochemical conditions during these tests, we feel that such an approach is justified. Figure 4.11 presents breakthrough curves obtained assuming a 35% reduction in source concentration for the following cases:

1. Assuming a sorption based retardation factor of 2;
2. Assuming matrix diffusion coefficient of 5×10^{-11} m^2/s;
3. Assuming a sorption based retardation coefficient of 2 and a matrix diffusion coefficient of 5×10^{-11} m^2/s.

While Figure 4.11 demonstrates that an increasingly better fit can be obtained with a more sophisticated model, e.g., the best fit is obtained using a sorption-based retardation of 2 and a diffusivity of 5×10^{-11} m^2/s, arguments could be made to accept any of the fits in Figure 4.11. For example, if the removal mechanism (e.g., precipitation) preferentially removed more strontium earlier in the test, the curve calculated assuming no matrix diffusion, would yield an improved match.

4.5 SUMMARY

From the preceding analyses it can be seen that acceptable fits could be obtained from a variety of mechanisms (provided some form of removal mechanism is assumed). Not surprisingly, it can also be seen that the goodness of fit increases with the increasing number of parameters available for the fitting. The analyses also demonstrates that it is crucial to determine conservative species behaviour in order to reduce uncertainty in sorption based retardation factors. Without definition of such behaviour, uncertainty will exist in both retardation factors and interstitial velocities.



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EFFECT OF INCLUDING A REMOVAL MECHANISM ON SR BREAKTHROUGH CURVES

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FIGURE 4.11

Finally, while the analyses has demonstrated that it is likely that at least one diffusion, one sorption and one removal type mechanism are operating, the analyses has not attempted to differentiate between the various possible types of diffusion/sorption that could be operational. This aspect is explored in more detail in the long term radionuclide transport calculations described in the following section.

5. LONG-TERM RADIONUCLIDE TRANSPORT CALCULATIONS

In Section 4, the Finnsjon tracer test data were analyzed and interpreted assuming that selected retardation mechanisms were in effect. This section examines the implications of extrapolating these findings to time frames that are more representative of the life expectancy of a high level nuclear waste repository - 10,000 years. It must be stressed that the purpose of this extrapolation is to examine the errors that may occur in such an exercise. A determination of the validity of such an exercise (i.e., extrapolating test data to significantly different spatial/temporal scales) is beyond the scope of the present work.

5.1 CONCEPTUAL MODEL DESCRIPTION

In order to assess the relative importance of retardation mechanisms in the context of the life of a nuclear waste repository, representative hydrogeologic conditions for such a facility must be established. Relevant parameters include travel paths, groundwater velocities and radionuclide source-term or release rates.

The hydrogeologic pathway(s) over which radionuclides are likely to reach the accessible environment is difficult to estimate. Because the repository will most probably be located at depths of between 0.5 and 1 km, the minimum path length can be expected to be on this order. For the purpose of these simulations we have selected a value of 1 km as representing the total path length.

Groundwater velocities are determined by the hydraulic conductivity of the fracture zone, the hydraulic gradient and the interstitial porosity. A reasonable estimate of the interstitial porosity can be obtained from the interpreted tracer test data. For the long-term radionuclide transport calculations a value of 0.0004 was used. Matrix porosities of 0.005 were also used in the calculations. The hydraulic gradients that will exist in the vicinity of a nuclear waste repository will vary over its life as

desaturation/resaturation and thermal loading will affect heads in the vicinity of the repository. Because of difficulties in quantifying these effects and because they are likely operative over a relatively short time frame compared to the total period of interest (INTERA, 1983; Andrews et al., 1986), it was felt that hydraulic gradients representative of natural conditions would most accurately reflect actual conditions. In crystalline rock formations such gradients may range from less than 0.0001 to 0.01 m/m, however most natural gradients are likely on the order of 0.001 m/m. The hydraulic conductivity of crystalline rock systems may vary significantly, from less than 10^{-12} m/s for sparsely fractured crystalline rocks at potential repository depths, to greater than 10^{-5} m/s for discrete open fractures or fracture zones at shallow depths.

In most performance assessments of geologic repositories in crystalline rocks (e.g., KBS, 1983) the most probable migration pathway for radionuclides from the waste repository to the accessible environment is via a permeable subvertical structural discontinuity such as a major fracture zone, fault zone or shear zone. For the generic repository considered in this study, such a permeable subvertical pathway is also assumed to exist. The hydraulic conductivity of this structural discontinuity and groundwater flow pathway was selected as 5×10^{-8} m/s similar to values reported for fracture zones at various locations in the Canadian Shield (Farvolden et al., 1988). This value of hydraulic conductivity was also selected because it provides a water travel time of 265 years which will allow an adequate assessment of matrix diffusion and other retardation effects over a 10,000 year time span.

A dispersivity of 100 m was assumed for these calculations which, for the assumed path length of 1 km, yields a Peclet number of 10. While these values are slightly different than those fitted from the Finnsjon tracer test analyses, they are in consistent with typical values reported in the literature for fractured crystalline rocks (Neretnieks, 1985).

The estimation of source release rates is extremely difficult to quantify since a variety of factors (e.g., canister corrosion, solubilities, etc.) will influence these rates. Because the primary objective of this study

is to quantify the effect of retardation mechanisms, we have elected to use a constant source term corresponding to a unit concentration. While this source rate may not reflect our best estimate of actual release rates it will, through its simplicity, aid in the interpretation of the long-term radionuclide migration calculations.

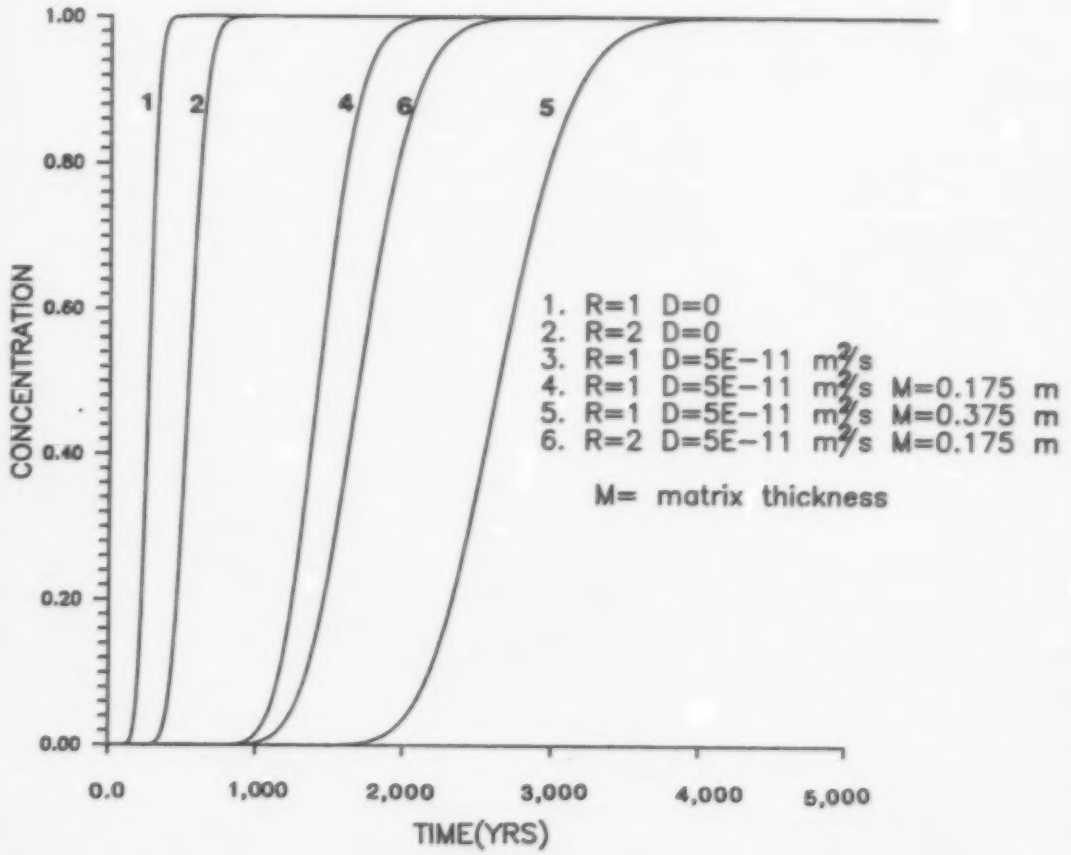
5.2 RESULTS

The SWIFT II model used to perform the tracer test interpretation was also used to perform the long-term radionuclide transport calculations. For these calculations a simple one-dimensional (cartesian) geometry was selected. As discussed previously, a constant Darcy flux of 5×10^{-11} m/s of unit concentration was input into one end of the system. The simulation results are discussed in terms of the breakthrough curve at the opposite end of system after migration along a 1 km flow path.

The cases examined as part of the long term radionuclide transport calculations are based on the interpretations of the Finnsjon tracer tests and include:

1. No sorption-based retardation or matrix diffusion;
2. A sorption-based retardation of two (matrix diffusion of zero);
3. Matrix diffusion using an effective diffusivity of 5×10^{-11} m/s^2 and an infinite matrix;
4. Matrix diffusion using a finite matrix of 0.175 m;
5. Matrix diffusion using a finite matrix of 0.375 m;
6. Matrix diffusion ($D = 5 \times 10^{-11}$ m/s^2), finite matrix and retardation in the fracture of two.

Case 1 represents the breakthrough curve for a non-sorbing and non-diffusing radionuclide. The breakthrough curve for such a hypothetical radionuclide is presented in Figure 5.1 as Simulation 1. For comparative purposes, Figure 5.1 also presents the breakthrough curves for the other five simulations. Although simulations were conducted over a 10,000 year period only



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BREAKTHROUGH CONCENTRATION AT 1 KM FOR LONG-TERM TRANSPORT CALCULATIONS

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FIGURE 5.1

the first 5,000 years of concentration time data were presented since in all cases but one complete breakthrough occurred over this time frame. Presenting the first 5,000 years of breakthrough data allows greater detail of the more relevant portions of the curves to be presented. The breakthrough curve for simulation 1 exhibits a classical "s" shape with $C = 0.5\ C_o$ corresponding to the water travel time of approximately 265 years. The curve may appear to be dominated more by plug flow (as indicated by the sharpness of the curve) than an advective dispersive process, however this is an artifact of the compressed time scale used in Figure 5.1. Simulation 1 likely represents the bounding behaviour of a hypothetical non-sorbing radionuclide released from a geologic repository because the simulation neglects the potentionally important retarding effects of matrix diffusion. This simulation was performed merely to demonstrate the physical properties of the system.

Simulation 2 uses the same conditions as Simulation 1 with the addition of a sorption-based retardation factor of 2 determined from the Finnsjon Sr^{2+} tracer test. The breakthrough curve for Simulation 2 is similar to Simulation 1 with the breakthrough of $C = 0.5\ C_o$ at about 530 years as predicted by a linear sorption isotherm. It is important to note when assessing the implications of this modeling that the interpreted sorption-based retardation are specific to the conditions of the Finnsjon tests. Sr^{2+} concentrations were high at 8300 mg/L and sorption isotherms and theory based on trace concentrations of sorbate may not be appropriate. In particular the retardation factor determined from the Finnsjon test, which is low in comparison to retardation factors interpreted from other Sr^{2+} field trace tests (Landstrom et al., 1982; Novakowski et al., 1985), may be attributed to saturations of sorption sites on the predominately calcite-infilled fractures at Finnsjon (Gustafsson and Klockars, 1984).

Because sorption-based retardation is not a significant process in the Finnsjon tests Simulations 1 and 2 represent the approximate two boundary cases for all other relevant sorption models that might consider kinetic effects or different sorption isotherms for the fracture.

Simulation 3 examined the effect of matrix diffusion on the breakthrough assuming a slab geometry and that a virtually infinite matrix thickness (10 m) was available for diffusion. No sorption-based retardation was employed for these simulations and the effective diffusion coefficient determined from the tracer test (5×10^{-11} m^2/s) was used. With this diffusion coefficient and large sink for radionuclides in the matrix, no breakthrough of radionuclides was detected at the end of the 1 km flowpath at the end of the simulation period (10,000 years).

Because the diffusion coefficients interpreted from the Finnsjon tests are much higher than most laboratory measurements, it is unlikely that they are representative of the diffusion properties of the bulk rock matrix. It is possible that such high diffusion coefficients reflect the enhanced diffusivity associated with weathered rock matrix and fracture infilling material that may coat the fracture surfaces. Because such weathered material is likely of minor thickness Simulation 4 was run to evaluate the resultant breakthrough curves for a finite slab thickness of matrix subject to diffusion. The matrix was assumed to use 0.175 m thick which corresponds to approximately twice the thickness of matrix penetrated during the Finnsjon tracer tests. No sorption-based retardation was considered in Simulation 4. The results of Simulation 4 show that the storage capacity of the matrix is completely exhausted at about 1,000 years.

Simulation 4 may also represent the breakthrough of a non-sorbing radionuclide that is subject to diffusional exchange between mobile and immobile porosities within a fracture plane. Such diffusional exchange was postulated for the Finnsjon tracer tests (Hodgkinson and Lever, 1983; Moreno et al., 1983) to explain the high diffusion coefficients interpreted from the I^- test. This behaviour is indistinguishable from matrix diffusion behaviour and will yield effective diffusivities and pore volumes that are virtually identical to matrix diffusion.

Simulation 5 investigated the sensitivity of non-sorbing breakthrough curves to the slab thickness of the matrix. In Simulation 5 the matrix thickness was increased to 0.375 m. The breakthrough curve shows high sensitivity to the thickness of matrix. According to Figure 5.1 increasing the matrix thickness from 0.175 to 0.375 m results in an increase in breakthrough time for 0.5 C_o concentration level from about 1400 years to about 2700 years.

Simulation 6 performed as part of the long-term transport calculations assumed a sorption based retardation of 2, a matrix diffusion coefficient of 5 x 10^{-11} m/s^2 and a finite matrix of 0.175 m. This corresponds to the combination of conditions which yielded the best fit to the Sr^{2+} tracer test at Finnsjon. The corresponding breakthrough curve is presented in Figure 5.1. By comparing this curve to that of Simulation 4, it can be seen that the sorption-based retardation, causes a delay in the arrival of the breakthrough curve. It is interesting to note that the magnitude of this delay is slightly concentration dependent being greater at higher concentrations than lower concentrations. This observation is presumably related to the fact that matrix diffusion is more significant at both higher concentrations and in retarded systems (since the time frame over which diffusion can act has been increased).

5.3 DISCUSSION

The long-term radionuclide migration predictions shown in Figure 5.1 provide a range of breakthrough times which can be partially characterized by the time for breakthrough of the 0.5 C_o concentration level. Each breakthrough curve shown in Figure 5.1 is based on retardation parameters derived from interpretation of the Finnsjon tracer tests. Simulations 1, 3, 4 and 5 are derived for non-sorbing radionuclides based on the I^- test data and Simulations 2 and 6 are based on the observed behaviour of weakly sorbed strontium. The simulations show that the 0.5 C_o breakthrough for non-sorbing species may vary from 265 to greater than 10,000 years and for weakly sorbing radionuclides from 530 to greater than 20,000 years. The upper time limit for breakthrough of sorbing species and non-sorbing species (i.e. Simulation 3) is uncertain because no breakthrough was observed at the end of the 10,000 year simulation period.

The results shown in Figure 5.1 are based on the interpretation of the Finnsjon tracer tests and therefore are specific to the I^- and Sr^{2+} species used as tracers and to the Finnsjon test conditions. Because different radionuclides have widely varying sorption and retardation behaviour and because different retardation behaviour has been reported even for the Sr^{2+} species used in the Finnsjon test, it may not be possible to extrapolate the results of this study to assessments of retardation behaviour of different radionuclides under different hydrogeologic and hydrogeochemical conditions.

The results of this study do demonstrate that it is necessary to quantify the relative contributions of all operative retardation mechanisms. This would include differentiating between retardation processes (e.g. sorption versus diffusion) as well as the various contributing components for a particular process (e.g. diffusion into matrix versus diffusion into immobile pore zones). For example, this study demonstrates that if the diffusion effects observed in field tracer tests are attributed to matrix diffusion versus immobile zones, widely varying radionuclide breakthrough curves will be obtained when extrapolating the field test data to larger spatial and temporal scales. The critical factor in obtaining a reliable extrapolation is determining the volume of pore space available for diffusion (i.e. matrix versus fracture dead zones). In most field tracer tests performed in fractures, it is not possible to obtain reliable estimates of this factor merely from analysis of the effluent breakthrough curves. Other methods, such as sampling of the fracture matrix rock system, may provide an indication of the penetration distance of tracers into the matrix. However the relatively short time frames of most tracer experiments suggest that tracers may only penetrate the matrix to a distance of a few centimetres. It remains to be demonstrated whether the large sink and therefore the potential retardation provided by a porous rock matrix up to several meters thick is accessible for radionuclides, particularly sorbing radionuclides which may preferentially be retained on the fracture surface.

6. CONCLUSIONS AND RECOMMENDATIONS

This study has demonstrated the uncertainties that may exist in the interpretations of sorbing and non-sorbing tracer tests and the resultant range of possible breakthrough curves that might be obtained from extrapolating the tracer tests to larger spatial and temporal scales representative of a geologic radioactive waste repository. The 0.5 C_o breakthrough times from a generic geologic repository considered in this study based on interpretation of the Finnsjon tracer tests range from 265 years to greater than 10,000 years for non-sorbing radionuclides and 530 years to greater than 20,000 years for weakly sorbing radionuclides such as Sr^{2+}.

The results of this study are highly dependent on the test conditions and particular sorbing species used in the Finnsjon tracer experiments. The Sr^{2+} tracer used in the Finnsjon tracer test was not strongly sorbed and was only weakly retarded with a retardation factor of 2. Because of this behaviour, the Sr^{2+} breakthrough curves in the tracer test are not sensitive to kinetic effects or different sorption isotherms and matrix diffusion is the dominant retardation mechanism active in the Finnsjon tests.

In spite of this, this study demonstrates that a wide range of retardation behaviour is possible through matrix diffusion effects and that characterization of the accessible pore space available for diffusion is required to refine field test interpretations and model predictions. This refinement is generally not possible for most field tracer tests in which only effluent breakthrough curves are available and only minor penetration of the matrix is likely to occur, particularly for sorbing radionuclides which may preferentially sorb to the fracture surface over diffusion into the matrix.

Other Sr^{2+} tracer tests (Landstrom et al., 1982; Novakowski et al., 1985) have shown a greater sorption and retardation than the Finnsjon tracer tests. It is likely that for these tests an even wider range of interpreted retardation parameters and resultant long-term radionuclide breakthrough curves would be obtained because sorption kinetics and different sorption isotherms are

likely important. The long-term radionuclide breakthrough curves extrapolated for these tests would likely occur much later in time, reflecting the larger retardation factors (15-100) reported for these tests. Future work should consider evaluation of these tests, particular those reported by Landstrom et al. (1982) for the Studsvik site, Sweden.

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